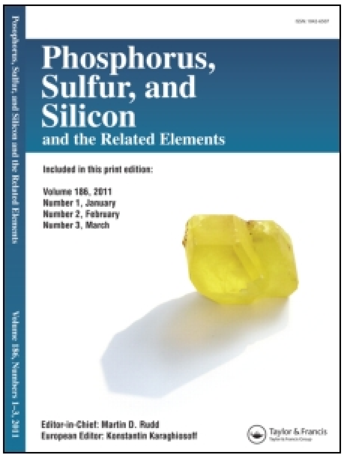

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Chemistry of P-Halogenoylids. Synthesis and Properties

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CHEMISTRY OF P-HALOGENOYLIDS. SYNTHESIS AND PROPERTIES

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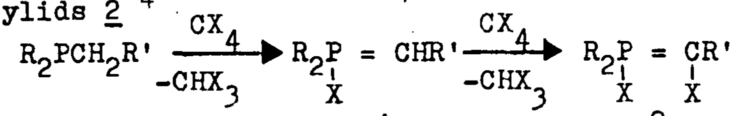
Abstract: Phosphor-carbon diad chlorotropic tautomerism is described. The reactions of P-halogenoylids with carbonyl compounds are discussed.

P-Halogenoylids are accessible reagents possessing high activity and various chemical properties.

The reaction of tertiary alkylphosphines with CX_4 (X = Br, Cl) is the most important method for the synthesis of P-halogenoylids.[1-3] Using this method one can prepare most of all conceivable P-halogenoylids with different substituents at the phosphorus and carbon atoms. The P-halogenoylids 1 react with excess of CX_4 to give C-halogenates P-halogenoylids 2[4]



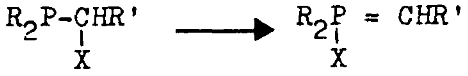
$$R_2PCH_2R' \xrightarrow[-CHX_3]{CX_4} \underset{X}{R_2P} = CHR' \xrightarrow[-CHX_3]{CX_4} \underset{X}{R_2P} = \underset{X}{CR'}$$

1 2

The dehydrohalogenation of halogenophosphoranes 3 by bases can also be used for the preparation of P-halogenoylids 4

$$\underset{\substack{n\,=\,1,\,2 \\ 3}}{R_{3-n}P(X)_{n+1}CHR'_2} \xrightarrow[B\cdot HX]{B} \underset{4}{R_{3-n}P(X)_n{=}CR'_2}$$

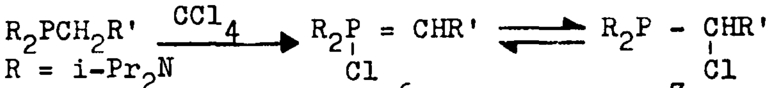
Some α-halogenoalkylphosphines 5 containing electron-withdrawing substituents R' readily rearrange into P-halogenoylids 1



$$R_2P\text{-}\underset{X}{CHR'} \longrightarrow \underset{X}{R_2P} = CHR'$$

5 1

At the same time, P-chloroylids 6 containing electron-donating groups R'= H, Me, Pr, i-Pr, OMe rearrange into α-chloroalkylphosphines



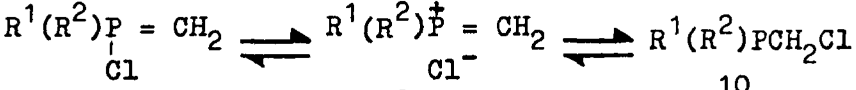
$$\underset{R\,=\,i\text{-}Pr_2N}{R_2PCH_2R'} \xrightarrow{CCl_4} \underset{Cl}{R_2P} = CHR' \rightleftharpoons R_2P - \underset{Cl}{CHR'}$$

6 7

The migration of the chlorine atom from the phosphorus atom to the α-carbon atom /the (P → C) chlorotropic shift/ is accompanied by decrease of the coordination number of the phosphorus atom.[5,6]

The ability to observe the P-chloroylids 6 by means of ^{13}C

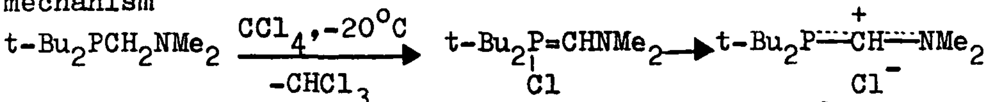
and ^{31}P NMR spectroscopy allowed to perform the detailed rate studies on their conversion into the α-chloroalkylphosphines 7. The kinetic studies have shown that the 6 → 7 rearrangement rate strictly obeis the first-order equation at different initial concentrations of the ylid 6 and at various temperatures. The first order rate constants for the 6 → 7 rearrangement increase very much with increasing the solvent polarity in the sequence: $C_5H_{12} < C_6H_6 < CH_2Cl_2 < CHCl_3 < CH_3CN$. The analysis of activation parameters in dependence on the temperature and medium have revealed the monomolecular mechanism of phosphorus-carbon diad chlorotropic rearrangement [7]



$$\underset{\mathbf{8}}{R^1(R^2)\underset{|\atop Cl}{P} = CH_2} \rightleftharpoons \underset{\mathbf{9}}{R^1(R^2)\overset{+}{P} = CH_2 \;\; Cl^-} \rightleftharpoons \underset{\mathbf{10}}{R^1(R^2)PCH_2Cl}$$

8 9 10

The dissociation of P-chloroylid with the P-Cl bond cleavage provides a phosphonium cation 9 which transformes into a chloromethylphosphine 10 via a nucleophilic attack of the chlorid-ion on the electronically deficient carbon atom. The transformation of P-chloroylid 11 containing dialkylamino groups at the α-carbon atom into a stable cation 12 isolated as a salt-like substance (m.p. 151°C) can be regarded [8] as an additional evidence for the proposed mechanism



$$t\text{-}Bu_2PCH_2NMe_2 \xrightarrow[-CHCl_3]{CCl_4,\,-20^{\circ}C} \underset{\mathbf{11}}{t\text{-}Bu_2\underset{|\atop Cl}{P}{=}CHNMe_2} \longrightarrow \underset{\mathbf{12}}{t\text{-}Bu_2P\cdots\overset{+}{C}H\cdots NMe_2 \;\; Cl^-}$$

11 12

The replacement of a dialkylamino group at the phosphorus atom by an alkyl group changes the direction of the chlorotropic rearrangement. In this case the chloromethylphosphonite 10 (R^1=t-Bu, R^2=Et_2N) converts into the P-chloroylid 8. Kinetic studies shown the first order for the 10 → 9 rearrangement too. Moreover, the rearrangement rate increases when the dissociating power of the solvent rises. Activation parameters for the 1,2(P → C) and 1,2 (C → P) chlorotropic rearrangements are identical. Evidently, these chlorotropic rearrangements proceed via the monomolecular mechanism.

NMR and chemical study of compounds 6,7 have shown that the rearrangement 6 ⇌ 7 is reversible and its direction depends on the nature of substituents at the α-carbon and phosphorus atoms, solvents, temperatures [7]:

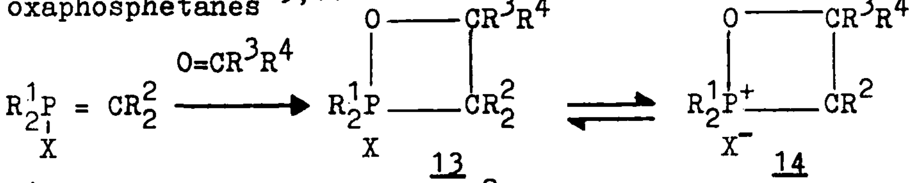
1. The electron-withdrawing substituents R' at the α-carbon atom shifts the 6 ⇌ 7 equilibrium towards the ylid form 6. The contents of the ylid form is about 20% (R^1=Cl)

in C_6H_6+20% wt $CHCl_3$ at +20°C.

2. In the crystallin state and in non-polar solvents the compounds 7 (R'= H, Alk or Cl) exist in the phosphine form. Howewer, in dissociating solvents (CH_3CN, $CHCl_3$ or CH_2Cl_2) the ylid and phosphine forms can be detected by NMR spectra.[2]

3. On heating the equilibrium shifts reversibly towards the phosphine form, on cooling - towards the ylid form. Compounds 7 undergo the reactions typical both for tervalent phosphorus compounds and P-chloroylids. Like the P-chloroylids, they add alcohols and phenols forming phosphonium salts, react with aldehydes to afford 2-chloroalkylphosphonates. At the same time, these compounds add sulfur to give thionophosphonates.[5-7]

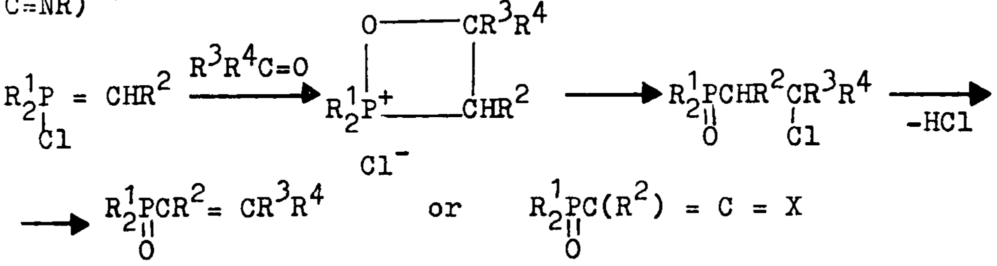
P-Halogenoylids react with aldehydes and ketones to afford stable /2 + 2/-cycloaddition products, 2-halogeno-1,2λ^5-oxaphosphetanes[9,10]



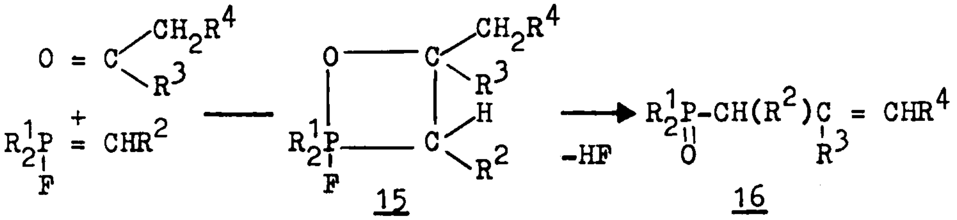
R^1= Alk, Ph, Alk_2N, AlkO; R^2= H, Alk, Ph, $SiMe_3$, Hlg; CR^3R^4= CHAlk, CHPh, $CAlk_2$, CAr_2, C = O, C = NPh, etc

2-Chloro- and 2-bromooxaphosphetanes 13 are dissociated with the formation of the cyclic phosphonium salts 14. 2-Fluorooxaphosphetanes 13 exist in non-dissociated state. The mechanism and stereochemistry of the /2 + 2/ cycloaddition reaction has been investigated by ^1H, ^{13}C, ^{19}F and ^{31}P spectra.[10,12]

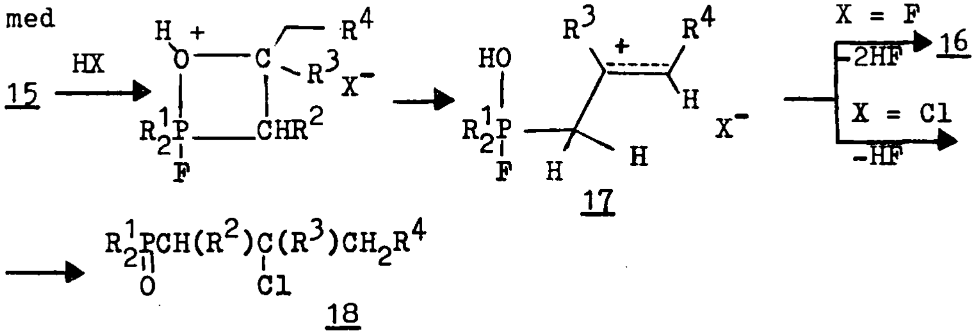
2-Chlorooxaphosphetanes 13 ⇌ 14 through formation of Arbusov rearrangement products yield the vinylphosphonates (R^3,R^4=H, Alk, Ar) or phosphorylated heterocumulenes (ketenes, thioketenes, ketenimines, CR^3R^4= C=X = C=0, C=S, C=NR)[12]



The 2-fluorooxaphosphetanes lose HF on heating and convert into the allylphosphonates 16.[9] The reaction has pronounced autocatalytic character as the hydrogen fluoride produced in the reaction catalysis the process. In the presence of Brönsted and Lewis acids (HF, HCl, $BF_3 \cdot Et_2O$) the reaction rate increases



The action of acids on the 2-fluorooxaphosphetanes 15 to produce an oxonium ion that easily transformes into a carbocation intermediate 17. The deprotonation of carbocation 17 via E_N1 mechanism gives preferably the more substituted alkene 16. The carbocation 17 can be trapped by hydrogen chloride. The interaction of 15 with an equimolecular amount of HCl in ether at -70°C produced 2-chloroalkylphosphonates 18 that via the nucleophilic attack of Cl^- on the positively charged carbon atom of intermediate 17 are formed



The reaction of P-halogenoylids with carbonyl compounds have been used in synthesis of natural compounds.

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