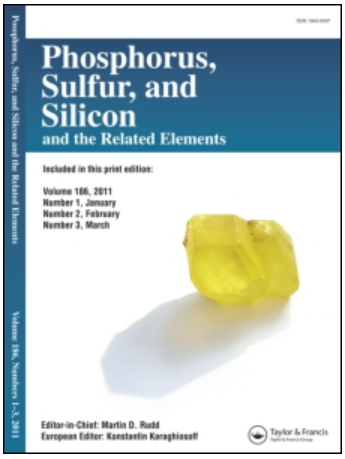


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Less Frequent Coordination States

To cite this Article (1983) 'Less Frequent Coordination States', Phosphorus, Sulfur, and Silicon and the Related Elements, 18: 1, 453 — 460
To link to this Article: DOI: 10.1080/03086648308076053
URL: http://dx.doi.org/10.1080/03086648308076053

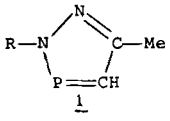
Phosphorus and Sulfur, 1983, Vol. 18 pp. 453-460
0308-664X/83/1801-0453/$18.50/0

DIELS ALDER REACTIONS INVOLVING THE P=C DOUBLE BOND IN DICOORDINATED PHOSPHORUS COMPOUNDS. X-RAY STRUCTURE. OXIDATION.

Y.Y.C. YEUNG LAM KO and R. CARRIÉ.
Groupe de Physicochimie Structurale, E.R.A. n° 389, Université de Rennes I, 35042 RENNES CEDEX.

Abstract : ENDO rule in Diels-Alder reaction with the $\diagdown P{=}C \diagup$ double bond.

1,2,3-diazaphosphole 1 react as a dienophile with 2,3 dimethyl butadiene. The (4 + 2) cycloaddition occurs at the $\diagdown P{=}C \diagup$ double bond and not the $\diagdown N{=}C \diagup$ double bond. An analogous arsenic compound reacts similarly while the nitrogen analogue does not. The phosphorus adducts are easily oxidized.



1

Compound 1 (R = MeCO) reacts also with cyclopentadiene. Already at room temperature, the kinetic (ENDO) adduct is in equilibrium with the thermodynamic (EXO) adduct (trapping experiment). The last one (more than 95 % at equilibrium) could be isolated pure and its structure has been determined by X-ray study. To our knowledge, this is the first time where the ENDO rule involving a nonheterodiene and a dicoordinated phosphorus dienophile is followed. Treated by sulfur in boiling benzene, the EXO isomer leads to two adducts sulfurized at the phosphorus atom (reaction of both ENDO and EXO adducts in equilibrium). NMR data (^{1}H, ^{13}C and ^{31}P) and mass spectrometry are in agreement with the structure of the products.

THE REACTIONS OF ADDITION TO DERIVATIVES OF 2-COORDINATED P AND As ATOMS

B.A.Arbuzov, E.N.Dianova. The A.M.Butlerov Chemical Research Institute, University, Lenin st.,18, 420008, Kazan, USSR

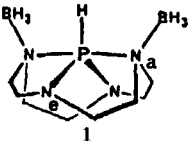
The reactions of diazaphosphols with diazocompounds and 2,5-diphenyldiazaarsole with diphenyldiazomethane and nitrons were thoroughly studied. The direction of this process was shown to depend on the structure of basic compounds and experimental conditions. Diphenyldiazomethane, methylphenyldiazomethane, diazofluoren add to P=C bond of diazaphosphols with the formation of the bicyclic heterocycles. In these compounds phosphorus atom occupies the top of 3- and 5- as well as 5- and 5-membered ring systems. Diphenyldiazomethane and nitrons was also shown to add to As=C bond of diazaarsols, forming bicyclic As-containing compounds.

The biphosphoric tricyclic compound was obtained by interaction of diazaphosphols with 2-diazopropane. The formation of this substance may be presented as 1,3-cycloaddition of diazaphosphols to diylid. The structure of the products was affirmed with the help of ^{1}H, ^{31}P, ^{13}C NMR and IR spectra as well as radiographic method.

COMPARATIVE STRUCTURAL STUDIES OF TWO ORIGINAL ADDUCTS OF DIBORANE : WITH THE "CLOSED" FORM OF CYCLENPHOSPHORANE AND WITH THE "OPEN" FORM OF CYCLAMPHOSPHORANE (CYCLAMPHOSPHANE).

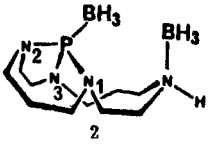
DUPART, J.M.*; GRAND, A.**; LE BORGNE, G.***; PACE, S.* ; RIESS, J.G.*. * Laboratoire de Chimie Minérale Moléculaire, E.R.A. n°473, Parc Valrose, 06034 NICE Cedex, France. ** Laboratoire Associé au CNRS n° 321, Département de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble, 85 X, 38041 GRENOBLE Cedex, France. *** Laboratoire de Cristallochimie, Université de Rennes, 35042 RENNES Cedex, France.

The structures of bis(borane)cyclenphosphorane **1** and bis(borane)cyclamphosphane **2** have been established by X-Ray diffraction. Both show many remarkable features : **1** provides the first example of a stable H_3B-N-P-N-BH_3 sequence, the arrangement of the five bonds around phosphorus is surprisingly close to a regular trigonal bipyramid. **2** is the first structure established for the "open" form of a tetracyclic tetraaminophosphorane. The diverse P-N bonds lengths, the pyramidal character of the nitrogen atoms and the conformation of the cycles will be discussed.



1

P-N_a : 1,87 Å
P-N_e : 1,65 Å
N-B : 1,60 Å
P-H : 1,25 Å



2

P-N_1 : 1,69 Å
P-N_2 : 1,65 Å
P-N_3 : 1,64 Å
N-B : 1,62 Å
P-B : 1,86 Å

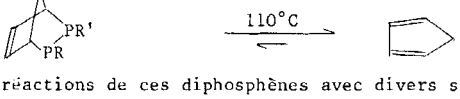
DIPHOSPHENES : SYNTHESE ET REACTIVITE

J. Escudié, C. Couret, J. Satgé, S.A. Thaoubane et H. Ranaivonjatovo
Université P. Sabatier, ERA 829 CNRS, 118 route de Narbonne, 31062 Toulouse cedex, France

Les diphosphènes RP=PR', molécules contenant deux atomes de phosphore dicoordonnés doublement liés, sont connus depuis peu. Un nouveau diphosphène stable, le bis[tris(triméthylsilyl)méthyl]diphosphène $(Me_3Si)_3C-P=P-C(SiMe_3)_3$ (1) a été synthétisé par action du tert-butyllithium sur la dichlorophosphine correspondante.

L'étude de la réactivité de ce diphosphène montre que, outre des propriétés découlant de l'insaturation, il peut être un excellent précurseur de phosphinidène $(Me_3Si)_3C-\bar{P}$.

Des diphosphènes symétriques ou dissymétriques ont pu également être obtenus par réaction d'échange entre phosphines disiliciées et dichlorophosphines et caractérisés par réaction de condensation sur des petits cycles ou de cycloaddition sur des diènes conjugués. Les adduits obtenus avec le cyclopentadiène apparaissent comme d'excellents précurseurs de diphosphènes instables mais de haute réactivité :



Les réactions de ces diphosphènes avec divers substrats insaturés seront présentées.

(1) C. Couret, J. Escudié, J. Satgé, Tetrahedron Lett. (1982), 23, 4941

LE PREMIER DIARSENE STABLE : LE BIS [TRIS(TRIMETHYLSILYL)METHYL]DIARSENE

par C. COURET[+], J. ESCUDIE[+], Y. MADAULE[‡], H. RANAIVONJATOVO[+] et J.G. WOLF[‡]

+ Université Paul Sabatier - Laboratoire de Chimie des Organominéraux - ERA CNRS n° 829

‡ Laboratoire de Synthèse et Physicochimie Organique - ERA CNRS n° 686
118, route de Narbonne - 31062 Toulouse cedex

Nous avons réalisé la synthèse du premier diarsène stable **1** :

$(Me_3Si)_3C\text{-}As{=}As\text{-}C(SiMe_3)_3$ **1**

$(Me_3Si)_3C\text{-}As(S)\text{-}As\text{-}C(SiMe_3)_3$ **2**

par action de $(Me_3Si)_3CLi$ sur $AsCl_3$ ou du tert-butyllithium sur $(Me_3Si)_3C\text{-}AsCl_2$. Ce composé purifié par chromatographie liquide sur colonne de silice [spectrométrie de masse : m/z = 612, UV 380 et 505 nm ; cryoscopie = 608 ; RMN ^1H δ = 0,30 , PF = 86-88° (déc)] réagit plus facilement avec le soufre que son homologue phosphoré : nous avons obtenu ainsi le premier diarsathiiranne **2** .

L'étude cinétique de l'évolution de ce diarsène en solution non polaire est en cours.

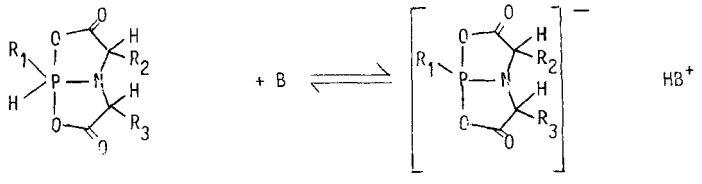
PHOSPHORANURES PREPARES A PARTIR D'AMINODIACIDES

B. GARRIGUES E.R.A. N° 926 - Université Paul Sabatier, 31062 Toulouse Cédex

L'action des bases (NEt_3 , DBU) sur les phosphoranes 1 conduit à un équilibre phosphorane $\rightleftharpoons$ phosphoranure. Cet équilibre est fortement déplacé vers la forme phosphoranure 2.

Ces phosphoranures manifestent des propriétés intéressantes vis-à-vis des réactifs électrophiles.

Dans le but d'obtenir des phosphoranures plus stables la synthèse de phosphoranes contenant un reste aminodiacide substitué a été réalisée(R_2 , R_3 = CH_3 , C_6H_5)



1 R_1 = CH_3 , C_6H_5 2 R_1 = CH_3 , C_6H_5

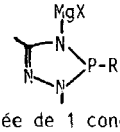
ACTION DES ORGANOMAGNESIENS SUR LES DERIVES DU TRIAZAPHOSPHOLE-1,2,4,3.

C. HADDAD, Th. N'GANDO M'PONDO, L. LOPEZ,G. CARUANA et J. BARRANS, Université P. Sabatier, E.R.A.-C.N.R.S. 926 118 Route de Narbonne 31062 Toulouse Cédex FRANCE

La synthèse d'alkylphosphine $AlkPY_2$ est souvent difficile. Nous avons pensé que la réaction d'organomagnésiens sur la double liaison P=N de phosphazènes du phosphore III pourrait être une méthode de synthèse de ces dérivés, selon la réaction :

$$-P{=}N- \;+\; RMgX \longrightarrow -\underset{R}{\overset{|}{P}} - \underset{MgX}{\overset{|}{N}}- \xrightarrow{HX} -\underset{R}{\overset{|}{P}}-NH-$$

Nous avons essayé cette réaction sur les triazaphospholes (T.A.P.). Celle-ci est différente suivant que l'on a affaire à des dérivés du triazaphosphole substitué en 2,5 ou en 1,5. Dans le premier cas nous avons isolé des composés d'addition 1



1 R = CH_3 , C_2H_5 , iPr, ... C_6H_5 ou de complexation $[TAP...MgX_2]$ dûs à l'équilibre : $2RMgX \rightleftharpoons MgR_2 + MgX_2$. L'hydrolyse (ou l'alcoolyse) ménagée de 1 conduit à la triazaphospholine correspondante.

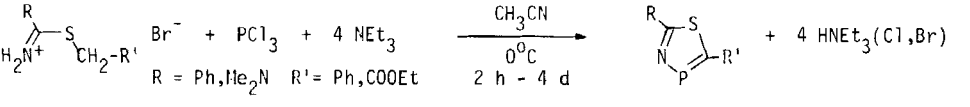
Dans le second cas on a seulement formation d'un complexe instable entre le réactif et le triazaphosphole sans ouverture de la double liaison.

L'étude est poursuivie sur d'autres composés du phosphore dicoordonné.

THE REACTION OF S-ALKYLATED THIOAMIDES WITH PCl_3: A ROUTE TO A NEW HETEROCYCLIC SYSTEM WITH DICOORDINATED PHOSPHORUS

Konstantin Karaghiosoff and Alfred Schmidpeter
Institut für Anorganische Chemie der Universität München, Meiserstraße 1, D-8000 München 2

The phosphaalkene group is highly stabilized as part of a fivemembered 6π heterocycle. Unfortunately just few types are accessible as yet. In looking for synthetic routes to new examples, we found that PCl_3 reacts with S-alkylated thioamides and triethylamine to give the novel 1,3,4-thiazaphospholes:

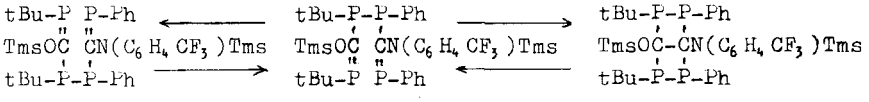


The synthesis strongly depends on proper conditions. Other conditions lead to different products.

The thiazaphospholes show ^{31}P chemical shifts of 250 to 300 to low field, i.e. in the range observed for other azaphospholes too. They are stable and rather insensitive compounds and they offer the unique possibility to compare the traditional heterocyclic members S and N and the newcomer P in the same ring and in the like situation, i.e. dicoordinated and offering a lone pair of electrons.

EVIDENCE OF THE FIRST EXAMPLE OF AN EQUILIBRIUM BETWEEN A TETRAPHOSPHAHEXADIENE AND A TETRAPHOSPHABICYCLOHEXANE. F. Knoll, W. Paulen and R. Appel, Anorg. Chem. Institut Universität Bonn, Gerhard-Domagk-Str., D-5300 Bonn, W.-Germany.

The target molecule, a mixed CF_3-probe attached O-silyl/N-aryl(silyl) carbon substituted compound was synthesized via a condensation reaction.

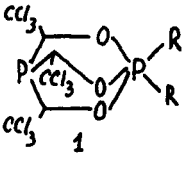


The molecule exists in solution in a dynamic equilibrium with it's 2+2 cyclo adduct as well as with itself, showing the phenomenon of the identical "Cope" rearrangment. The two different compounds can be isolated and characterized by x-ray determination and ^{31}P-solid-state-n.m.r.. The two different equilibria can be detected by ^{1}H,^{19}F,^{13}C and ^{31}P high resolution n.m.r.

The thermodynamic data will be given and discussed in comparison to analog pure organic systems.

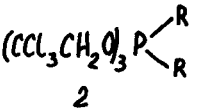
ACYCLIC AND BICYCLIC ALKOXYPHOSPHORANES WITH ELECTRONWITHDRAWING SUBSTITUENTS. L. N. Markovski, A. V. Solov'ev, Yu. G. Shermolovich. Institute of Organic Chemistry Academy of Sciences of Ukrainian SSR, 252660, Kiev 94, USSR.

The comparative study of bicyclic (I) and acyclic oxyphosphoranes (2), derived from 2,6,7-tris(trichloromethyl)-1,4-diphospha-3,5,8-trioxabicyclo(2,2,2)octane and tris(2,2,2-trichloroethyl)phosphite respectively, have been carried out with the aim to investigate bicyclooctane structure influence on thermal stability and reactivity in pentacoordinated phosphorus compounds. The presence of caged frame has been shown to stabilize the phosphorus pentacoordinate state in bicyclic dihalogenophosphoranes (1) compared to acyclic ones (2).



1

R: Cl, Br, C_6H_5O, CCl_3CH_2O.



2

QUELQUES RESULTATS RECENTS DANS LA CHIMIE DES PHOSPHENIUMS

Marie-Rose MARRE, Michel SANCHEZ, Jean-François BRAZIER, Jacques BELLAN et Robert WOLF
Equipe de Recherche Associée, n° 926 C.N.R.S., Université Paul Sabatier, 118 route de Narbonne 31062 Toulouse Cédex (France)

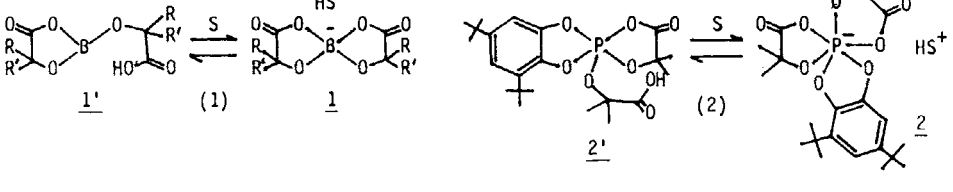
Les cations dicovalents du phosphore $[-P-]^+$, envisagés depuis très longtemps ($Cl-\overset{+}{P}-Cl$ dans la réaction de Friedel et Craft), observés communément en spectrographie de masse, clairement caractérisés en 1972 (Fleming et coll. Hutchins et coll.) sont actuellement l'objet d'études originales et intéressantes (Cowley et coll., Paine et coll., Parry et coll. etc...).

Sur 4 exemples de type $[>N-P-N<]^+$ nous montrons que l'action des azotures $R-N_3$ conduit aux iminophosphéniums $[R-N=P-(N<)_2]^+$. Les données spectrographiques détaillées sur plusieurs des cations obtenus (RMN de ^1H, ^{31}P, ^{13}C et ^{27}Al) démontrent la structure de ceux-ci. Nous montrons que la réaction passe bien par le cation phosphénium et non par le dérivé tricovalent du phosphore $(>N)_2P-Cl$ qui a servi à le préparer. (Ce qui reviendrait alors à une réaction de Staudinger ordinaire). De la même manière, l'action du soufre sur les phosphéniums conduit aux thiophosphéniums. (Marre et coll. P et S, 1982, 13, p. 327. Sanchez et coll. P et S, 1983, 14, p. 331).

SPIRANNES DU BORE ET γ HYDROXYPHOSPHORANES - TAUTOMERIE ET ACIDITE

A. MUNOZ, L. LAMANDE ET D. BOYER - ERA N° 926 - UNIVERSITE PAUL SABATIER - 118 ROUTE DE NARBONNE - 31062 TOULOUSE CEDEX - FRANCE.

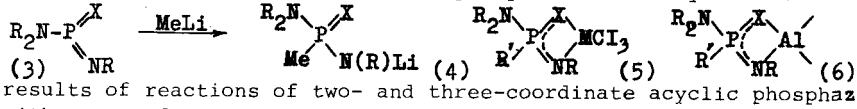
En solution dans le THF ou CD_3CN, les borates 1' existent sous la forme d'un équilibre (1). Dans le DMF ou le DMSO, ce dernier est déplacé totalement, d'après la RMN de ^{11}B, vers le spiranne 1. L'équilibre (1) est comparable au système (2). Dans le toluène, celui-ci est entièrement déplacé, d'après la RMN de ^{31}P, vers le phosphorane 2', alors qu'en solution dans le DMF ou le DMSO, c'est la forme 2 qui est seule présente. Les pKa des composés 1 et 2, déterminés par titration potentiométrique dans le DMSO et le DMF, correspondent à des acides au moins aussi forts que l'acide picrique. Le remplacement du ligand α hydroxyacide par le ligand éthanediol amène une baisse importante de l'acidité.



1' 1 2' 2

THE REACTIONS OF TWO- AND THREE- COORDINATE ACYCLIC PHOSPHAZENES WITH ORGANOMETALLIC REAGENTS. V.D.Romanenko, V.I.Schul'gin, L.N.Polyachenko, E.O.Klebanskii. Institute of Organic Chemistry Academy of Sciences of Ukrainian SSR, 252660, Kiev, USSR.

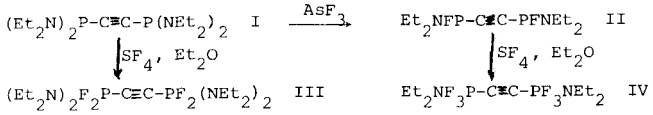
The aminoiminophosphines >N-P=N< (1) are reactive toward a serie of such strong nucleophiles as alkyl lithiums. Treatment of 1 with MeLi to afford the ionic species [>N—P(Me)—N<]$^-$ Li^+ in which methyl group is directly attached to the phosphorus. An extension of this approach to functionalized alkyl lithiums such as $(Me_3Si)_2CClLi$ allowed as to prepare new three-coordinate phosphazenes **3** [X=C(SiMe$_3$)$_2$].- Alkyl- or aryl lithiums attack phosphazenes 3 (X=NR,S,Se) at phosphorus to give compounds **4** which in turn can react with metal halides (M=Sn,Ti) to give ring coupled species **5**. -Organolithiums reagents react with phosphazenes 3 to yield **6**.



The results of reactions of two- and three-coordinate acyclic phosphazenes with compounds containing M-Si bond (M=Li,Al,Hg) will also be presented.

BIS(PHOSPHORANYL)ACETYLENES E. Fluck and J. Svara Gmelin-Inst. f. Anorg. Chemie u. Grenzgebiete d. Max-Planck-Gesellschaft, Varrentrappstr. 40/42 D-6000 Frankfurt a.M.90 Inst. f. Anorg. Chem. d. Univ. Pfaffenwaldring 55, D-7000 Stuttgart 80

In bis[bis-(diethylamino)phosphanyl]acetylene I [1] one diethylaminogroup on each phosphorus atom can be exchanged for fluorine by AsF_3 to give compound II. By oxidative fluorination of I and II with SF_4 the corresponding bis(phosphoranyl)acetylenes III and IV are obtained.



III is a colorless solid, m.p. 107,5-109,5 °C (space group $I4_1/a$, tetragonal, a=b=14,053, c=12,360 Å; Z=4; C≡C=1,202; C-P=1,778; P-F=1,631 Å; [2]).
The result of the reaction

$$Cl_2P\text{-}C{\equiv}C\text{-}PCl_2 + SF_4$$

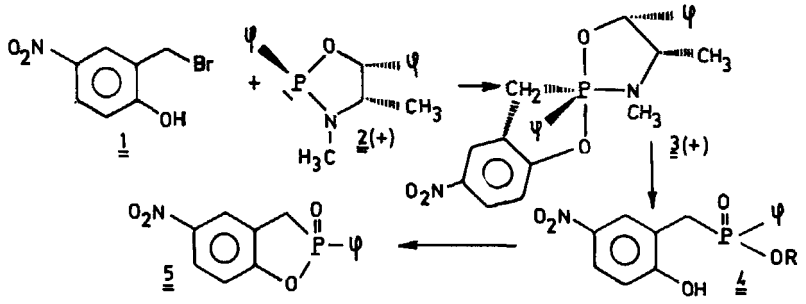
is reported.

[1] W. Kuchen and K. Koch, Z. Naturforsch. 25b, 1189 (1970); Z. anorg. allg. Chem. 394, 74 (1972).
2 E. Fluck, J. Svara, and J.J. Stezowski, Chem.-Ztg. 106, 439 (1982).

NEW CHIRAL SPIRO-BICYCLIC PHOSPHORANES

Francine ACHER[a], Sylvain JUGE[b] et Michel WAKSELMAN[a]
a) CERCOA-CNRS Thiais b) Laboratoire de Chimie Générale, CNAM, Paris.

The reaction of 2-hydroxy-5-nitro-benzyl bromide 1 with a chiral 2-phenyl-oxaza-phospholidine 2 derivated from (+) or (-) ephedrine gives a chiral five five spiro-bicyclic phosphorane 3(+) or 3(-) ($\delta^{31}P$ = -28.6). The transformation of 3 into 4 and then 5 is studied.



THE ESTER ALKYL EXCHANGE REACTION OF QUINQUEVALENT PHOSPHORUS ESTERS WITH ALKYL HALIDE IN THE PRESENCE OF SODIUM HALIDE.

Yuan Chengye, Ye Weizhen and Zhou Guo-wei. Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, CHINA.

Various types of quinquevalent phosphorus esters undergo ester alkyl exchange reaction with alkyl halide in the presence of sodium bromide under mild conditions. The experimental data undoubtedly indicated that sodium halides accelerate the reaction. This ester alkyl exchange reaction was evidently influenced by the structure of both phosphorus esters and alkyl halides as well as by the nature of the metal ions in inorganic halides. In contrast with the reaction without sodium halide, the alkyl phosphinate is more reactive than corresponding phosphonate and phosphate by treatment with alkyl halide in the presence of sodium halide. This is consistent with the highly nucleophilicity of $>P(O)O^-$ as leaving group. The reactivity of butyl halides was decreased in the following order: n-BuBr > i-BuBr > s-BuBr > t-BuBr. Alkyl iodide was proved to be more reactive than the corresponding bromide and chloride. However, the use of iodide is limited by the formation of alkene resulted from the elimination of HI under reaction conditions. These structure effects show the general charasteristics of a nucleophilic substitution reaction. A reaction mechanism involving the formation of sodium salt intermediate was proposed based on the conception of HSAB principle. The mentioned reaction may, however, be served as a convenient method for the preparation of mixed esters of quinquevalent phosphorus acids.