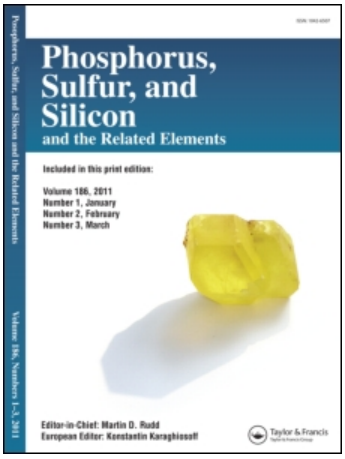

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COMPETITIVE ADDITION AND CYCLOADDITION OF LOW COORDINATED ORGANOPHOSPHORUS COMPOUNDS TO ALKOXY- AND AMINOALKYNES.

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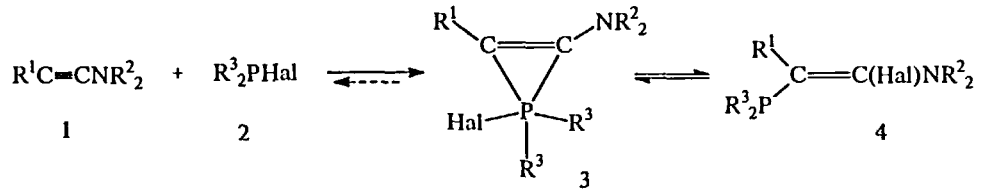
Abstract Reactions of two- and three coordinated organophosphorus compounds with nucleophilic alkynes can proceed as competitive addition, [2+1]-, and [2+2]- cycloaddition reactions. Ring-chain tautomerism for phosphirenes and isomeric alkenylphosphines has been observed.

Recently the investigations carried out in our laboratory have shown that the addition of phosphorus halides to triple bond of ynethers leads to the formation of β-halogeno-β-alkoxyalkenylphosphines, phosphirenes, phosphorus(III) substituted ketenes and other compounds. Here we report on the reactions of phosphorus(II) and (III) halides and other phosphorus (II) compounds with nucleophilic alkynes which proceed as competitive addition, cycloaddition and insertion processes.

The reaction of halogenophosphines **1** and ynamines **2** leads to phosphirenes **3**, halogenoalkenylphosphines **4** or their mixtures depending on the nature of reagents and solvents used. The reaction of iodo- or bromodiisopropylphosphines with ethyldiethylaminoacetylene or the reaction of chlorodiisopropylphosphine with ynamines with R^1 or R^2 = i-Pr forms exclusively **3**. In the case when only one of R^3 substituents in starting **2** is electron-withdrawing group (R^3=Cl, Ph) the sole isomer of alkenylphosphine **4** is formed. However in most cases we have observed competitive formation of **3** and **4**.



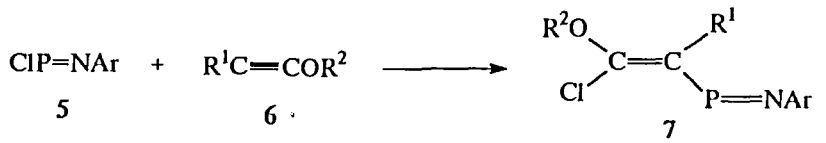
We have shown that ring-chain tautomerism for **3** and **4** takes place. For example, for **3** and **4** (where R^1=R^2=Et, R^3=i-Pr, Hal=Cl) the mixture contains 10% of **3** in pentane, 50% of **3** in benzene and 100% of **3** in dichloromethane. The equilibrium depends on the nature of halogen atom, electron and steric properties of substituents at

triple bond and phosphorus atom and on solvents used. The content of **3** increases in following sequences : R^1=Me<Et<i-Pr; R^2=Et<i-Pr; R^3=Et<c-C_6H_{11}=i-Pr<(i-Pr,t-Bu); Hal=Cl<Br=I. Thus the increase of steric hindrances and electron-donating properties of substituents leads to the increase of stability of **3**.

Solvation of **3** is very important for the position of equilibrium between **3** and **4**. Obviously P-Hal bond in **3** is partly ionic and the extent of ionization increases both in polar solvents and in the sequence Hal=Cl<Br<I. A strong upfield shift of ^{31}P resonance signal of chlorophosphirenes in pentane or benzene (*ca* 17-25 ppm) as compared to dichloromethane and upfield shift of ^{31}P resonance signal of chlorophosphirenes (*ca* 9-26 ppm) as compared to bromo- and iododerivatives confirm the decrease in P-Hal bond ionization and the increase in phosphorane character of **3** in the sequence I<Br<Cl. Thus easier ionization of P-Hal bond in **3** results in the increase of stability of phosphirenes.

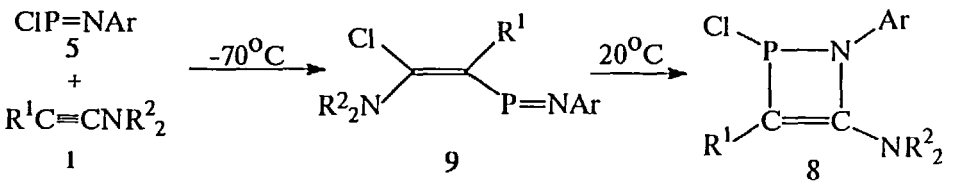
NMR ^{13}C data of **3** show that these molecules exist in the state of distorted bipyramid at phosphorus atom with apical P-Cl and P-C(NR_2) bonds. NMR ^{13}C data for **4** show that one isomer is formed in most cases. However thermodynamically controlled mixture of 70-80% major and 30-20% minor isomers was observed for several compounds due to easy cis-trans isomerization of α-chloroenamines. One of us thoroughly elaborated the method of establishing the configuration of the double bond in P(III)-substituted alkenylalkyl ethers. This method is based on the difference in the values of ^{2}J(PC) of olefin carbon atom for different isomers. Later this method proved to be applicable also for P(III)-substituted enamines. We assume that this method can be applied to compounds of type **4**, and the major isomer of **4** has E-configuration of the double bond.

The reaction of P-chloroiminophosphine **5** with 1-alkoxyalkynes **6** leads to 1,2-addition to triple bond with the retention of two-coordinated phosphorus, and previously unknown 1-aza-2-phosphabutadienes-1,3 **7** are formed in quantitative yields.

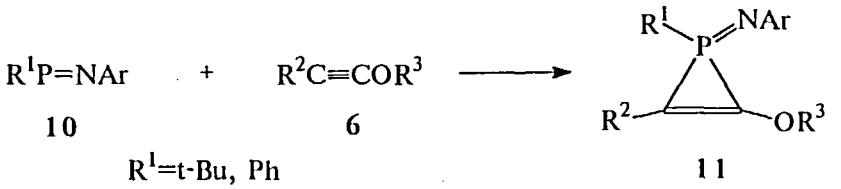


Ar=2,4,6-tri-tert.-butylphenyl

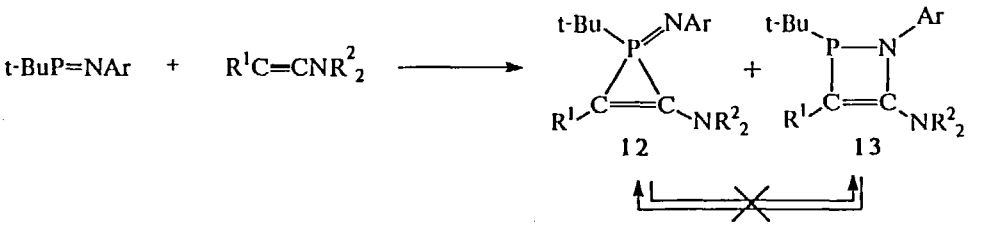
In most cases 1-aza-2-phosphabutadienes **7** are formed as pure Z-isomers. The reaction of P-chloroiminophosphine **5** with 1-aminoalkynes **1** leads to 1,2-azaphosphetines **8** in high yields, and 1,2-addition to triple bond with formation of **9** takes place here as an intermediate process.



According to calculations made by Schoeller and Niecke iminophosphines can react with unsaturated compounds either as carbene analogs or as alkene analogs which makes possible [2+1]- and [2+2]-cycloaddition reactions to proceed. We have investigated the reactions of iminophosphines **10** with non-terminal 1-alkoxyalkynes and demonstrated the formation of [2+1]-cycloaddition products **11**.

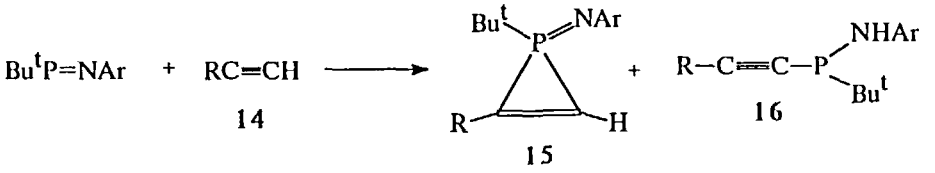


Nevertheless the reaction of P-tert.-butyliminophosphine with 1-aminoalkynes generally produces the mixture of phosphirene **12** with azaphosphetine **13**.



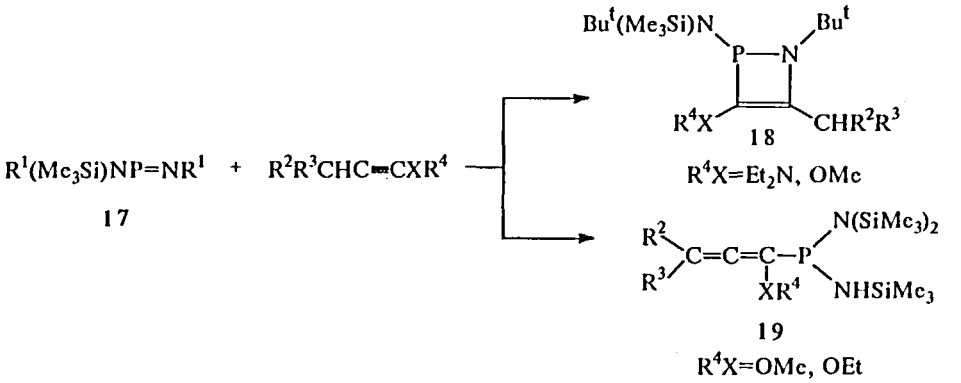
The formation of these products is a result of competitive [2+1]- and [2+2]-cycloaddition reactions. The increase of spatial hindrances of R^1 group as well as the use of polar solvents results in preferable formation of azaphosphetine **13**, the increase of steric hindrances at nitrogen atom of amino group results in exclusive formation of phosphirene **12**.

The reaction of P-tert.-butyliminophosphine with terminal non-activated alkynes **14** produces not only expected phosphirenes **15** but also less or more amount of acyclic P(III)-substituted alkynes **16** due to competitive reactions of [2+1]-cycloaddition and addition of C-H bond of alkyne to P=N bond.

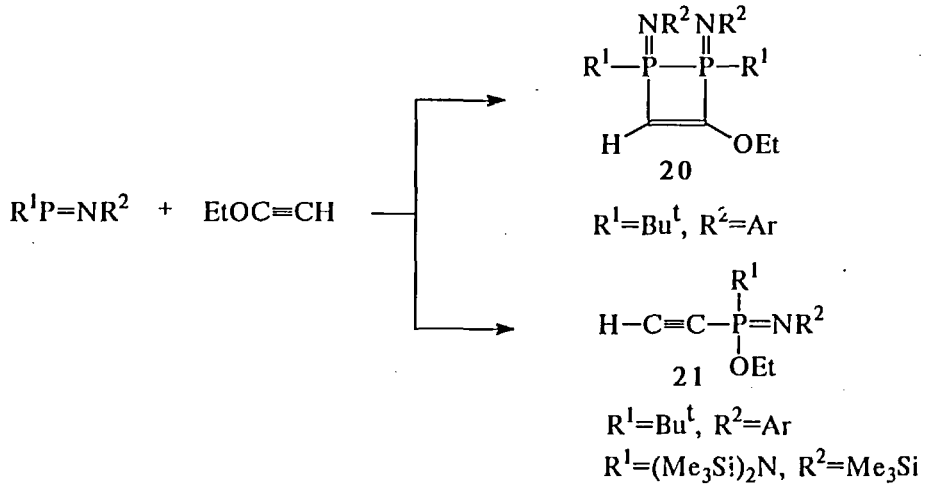


Amidoiminophosphenites **17** react with 1-aminoalkynes to form 1,2-azaphosphetines **18**. The reaction is regioselective and in this case regioselectivity is opposite to that in the

addition of P-tert.-butyliminophosphine to 1-aminoalkynes. The reaction of amidoiminophosphenites **17** with 1-alkoxyalkynes gives rise to new interesting products - azaphosphetines **18** or allenes **19**.



Unexpected results have been obtained when terminal ethoxyacetylene was used in the reactions with iminophosphines. P-tert.-butyliminophosphine and ethoxyacetylene in pentane solution furnished 1,2-diphosphetene **20** whereas in polar acetonitrile substituted acetylene **21** was found to be the major product. This unusual formation of acetylene *via* formal cleavage of C(sp)-O bond has been also observed in the reaction of amidoiminophosphenite with ethoxyacetylene.



Some of presented results were published by us in *Mendeleev Commun.* 1993. N2. P. 68-70, *Tetrahedron Lett.*, 1993, Vol.34, N8, pp. 1331-1334,.and in six articles in *J. of Organic Chemistry (Russia)* in 1994-1995.