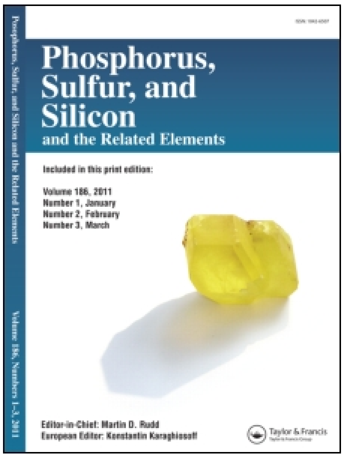

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Phosphorus (III) - and Phosphorus (IV)-Substituted Alkoxyacetylenes as New Synthons in Phosphororganic Synthesis

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PHOSPHORUS(III)- AND PHOSPHORUS(IV)-SUBSTITUTED ALKOXYACETYLENES AS NEW SYNTHONS IN PHOSPHORORGANIC SYNTHESIS

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The diheterosubstituted acetylenes of EC≡COR type, where E is Si, Ge, Sn, B, possessing an increased reactivity both in reactions with electrophilic reagents and fragmentation processes, are extensively investigated in the Moscow University. At the same time phosphorylated alkoxyacetylenes have gained less attention. The main purpose of this work was the synthesis of previously unknown phosphorus(III)-substituted alkoxyacetylenes (I), investigation of their stability, properties and applications in phosphororganic syntheses.

The synthesis of the I was accomplished by the reaction of phosphinehalides with LiC≡COR.

$$X_2PCl + LiC{\equiv}COR \longrightarrow X_2PC{\equiv}COR \qquad (I)$$

X = i-Pr, t-Bu, Ph, C_6F_5, OAlk, NPr_2-i; R = Me, Et, Bu, Ph.

The stability of I is defined by the nature of subsituents at the phosphorus atom and in the alkoxygroup. In the case of R=Et the phosphines I are instable. Phosphines with secondary, tertiary or C_6H_5 substituents at phosphorus atom, decreasing its nucleophilicity due to steric or electron effects, could be isolated in an individual state. Alkoxyethynylphosphonites (X = OAlk) and -diamidophosphonites exist only in solutions (with the exception of sterically hindered I with X = i-Pr_2N).

^{13}C NMR parameters give evidence of phosphorus atom electronacceptor influence and essential contribution of boundary structures (B) and (C) in electron density delocalization in alkoxyethynylphosphine molecules.

$$R_2PC{\equiv}COR \ (A) \longleftrightarrow R_2PC^{-}{=}C{=}O^{+}R \ (B) \longleftrightarrow R_2\bar{P}{=}C{=}C{=}O^{+}R \ (C)$$

Strong shift of electron density in I should lead to increase in nucleophilicity of phosphorus atom and oxonic character of oxygen atom. As a consequence alkoxyethynylphosphines should undergo intermolecular transmutations of different kinds. In many cases that appears to be the cause of its unstability.

In fact we have found such kind of transmutations: methoxyethynylphosphines rearrange at high speed into isomeric ketenylidenphosphoranes with quantitative yields.

$R_2PC\equiv COMe \longrightarrow R_2MeP{=}C{=}C{=}O$ (II)

This rearrangement can be accelerated by the addition of electrophilic catalysts. Equimolar amount of alkylhalides quantitatively transforms phosphines I into II.

$X_2PC\equiv COR + R'Hal \xrightarrow{20^{o}C} X_2P(R){=}C{=}C{=}O$ (II)

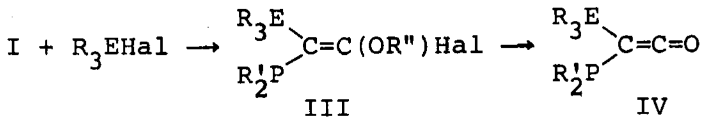
X = i-Pr, t-Bu, OMe, NPr_2-i; R = Me, Et, Bu;

R' = R, Allyl, $PhCH_2$

Rearrangement of I into thermodynamically stable isomers II containing heterocumulenic bond system appears to be a new transformation. Such rearrangement was unknown both for derivatives of tricoordinated phosphorus and for other element-substituted ethynylethers.

Versatile synthetic applications of I are based on the presence of several nucleophilic centres in their molecules. The reaction pathway is determined by the nature of electrophile, electron and steric properties of substituents near phosphorus atom and in the alkoxy-group. The reaction of $t\text{-}Bu_2PC\equiv COEt$ with EtSCl (soft electrophile) proceeds at the soft nucleophilic centre of phosphorus atom and results in $t\text{-}Bu_2P(SEt){=}C{=}C{=}O$.

Reactions of phosphines I with hard electrophiles, Si and Ge halides, proceed with formation of products with element-carbon bond: vinyl ethers III or elementphosphorsubstituted ketenes IV.



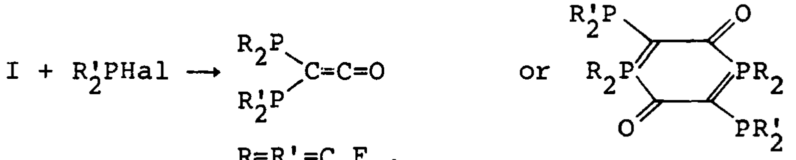
$$I + R_3EHal \longrightarrow \begin{matrix} R_3E \\ R'_2P \end{matrix}\!\!>\!C{=}C(OR'')Hal \longrightarrow \begin{matrix} R_3E \\ R'_2P \end{matrix}\!\!>\!C{=}C{=}O$$

III IV

R = Me, Et; R' = i-Pr, t-Bu, C_6F_5; R" = Et, Bu; Hal = Br,I.

The previously unknown ketenes IV are stable in the presence of bulky or electron-accepting substituents. In other cases (R' = i-Pr) they easily dimerize into a complex mixture.

The addition of dialkyl(aryl)phosphinehalides allows to synthesize two more new types of phosphororganic compounds: diphosphorsubstituted ketenes and diphosphosubstituted heterocycles V. The reaction pathway is dependent on the nature of substituents at the phosphorus atom.



V

R=R'=C_6F_5,
R=t-Bu, R'=i-Pr

R,R'=Et, i-Pr, Ph;
R'=t-Bu, C_6F_5, PhO.

Compared with P(III)-substituted alkoxyacetylenes, the P(IV)-substituted analogs are less accessible compounds. The attempts to obtain them either by the reaction of P(IV)-acids halogenanhydrides with lithium alkoxyacetylenides or by oxidation of phosphines I were unsuccessful. Only the reaction of phosphines I with sulfur leads to satisfactory preparation of thiooxides VI.

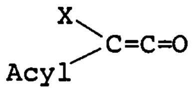
$$R_2PC{\equiv}COR' + S \longrightarrow \underset{VI}{R_2P(S)C{\equiv}COR'} \xrightarrow{20^o} \underset{VII}{R_2P(SR')=C=C=O}$$

One of the reasons for the low stability of the compounds is phosphorus containing electronacceptor substituent causing strong polarization of molecule. This leads to enhancement of alkoxy group alkylation ability and more easy isomerization of VI into ketenylidenphosphoranes in comparison to P(III) analogs. Easy isomerization of VI into VII suggests that the moving force of rearrangement is not the increase in phosphorus atom coordination number, but a formation of energetically more advantageous heterocumulated bond system.

Alkoxyethynylphosphine thiooxides react easily with different electrophilic reagents yielding products with electrophile-sulfur and electrophile-carbon bonds.

VI + AlkI → VII → 2+2 dimerisation

VI + AcylCl → Acyl(X)C=C(Cl)OR' →



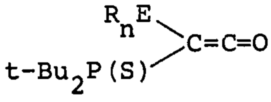
$\overset{X}{\underset{Acyl}{>}}C=C=O$

Acyl = Ac, t-BuCO; X = t-$Bu_2P(S)$

Phosphorylated acylketenes are useful as synthons for different types of heterocyclic compounds synthesis.

Reaction of the VI with elementhalides of Si, Ge and P leads to the formation of series of elementphosphorus(IV)-substituted ketenes. Although these compounds could be potentially tautomeric when R_nE fragment migrates to oxygen or sulfur atoms, we have not succeeded in finding convincing evidence of rearrangements.

VI + R_nEHal →



$\overset{R_nE}{\underset{t\text{-}Bu_2P(S)}{>}}C=C=O$

R_nE=Me_3Si, Et_3Si, Me_2t-BuSi, i-Pr_3Si, Me_3Ge, Et_3Ge, Ph_3Ge, i-Pr_2P.

We have synthesized complexes of phosphines I with chromium and tungsten carbonyles. These compounds are stable, do not isomerize with formation of ketenic group and have less reactivity compared to initial phosphines. With hard electrophiles in polar solvents, however, they form phosphorus-substituted ketenes in coordination sphere of transition metal.

P(IV)-Substituted alkoxyacetylenes are active in reaction with such nucleophiles like amines and alcohols. That opens a new approach to phosphorylated ketenacetals, -aminales and carbonic acids.

VI + XH → $R_2P(S)CH=C(OR)X$

R = i-Pr, t-Bu; X = R'_2N, OR'.

Thus, phosphorylated alkoxyacetylenes prove to be useful reagents for the synthesis of new types of phosphororganic compounds.

The principal results of this work were published in

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