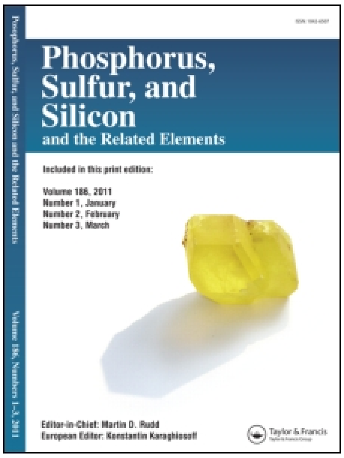

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New Unusual Reactions in the Chemistry of Unsaturated Organophosphorus Compounds

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NEW UNUSUAL REACTIONS IN THE CHEMISTRY OF UNSATURATED ORGANOPHOSPHORUS COMPOUNDS

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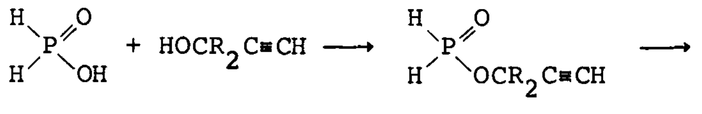
The paper presents the authors' recent investigations on unsaturated organophosphorus compounds and comprises: (1) methods of C-P bond formation, (2) construction of C-P bonded unsaturated compounds, (3) their isomerizations and (4) reactions directed to the formation of C-functional derivatives.

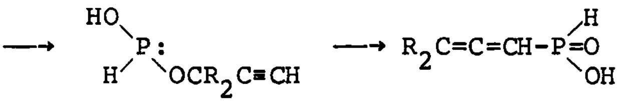
1. Methods of C-P Bond Formation.

Arbusov reaction of trialkyl phosphites with haloalkynes opened a new route to the synthesis of acetylenic phosphonates as well as attracted the investigators attention to the nucleophilic substitution of halogene at sp-hybridized carbon atoms. The most important compounds of this type are chloro- and bromoethyne phosphonates formed by the action of dihaloethynes upon phosphites. These polyfunctional compounds may interact via triple bond opening and/or halogene substitution. The latter pathway results in the formation of different phosphonates and diphosphonates (1):

$$\underset{\textbf{1}}{X\text{-}C{\equiv}C\text{-}P(O)(OAlk)_2} \qquad X\text{: Cl, Br, AlkS, ArS, ArO, NAlk}_2\text{, t-BuPH, P(O)(OAlk)}_2$$

The study of acetylene-allene rearrangement of propargyl phosphites permitted us to propose two new ways of synthesis of unsaturated phosphonates. The first is a hydrophosphoryl acetylene - allene conversion which probably includes P(IV)-P(III)-P(IV) transformation:





$$\longrightarrow \mathrm{HO(H)P{:}OCR_2C{\equiv}CH} \longrightarrow \mathrm{R_2C{=}C{=}CH{-}P({=}O)(H)(OH)}$$

2

The second one is a rearrangement of chloromethyl- or alkoxymethyl-propargylphosphites resulting in the formation of corresponding substituted allenes. The latter may be converted to conjugated dienes (Ch. 3).

Homolytic addition of phosphorus trihalides to alkenes and alkynes enables preparation of unsaturated phosphines, chloroalkene phosphonates and some phosphonoprenes. Our investigations include two homolytic reactions: oxydative phosphonation and photoinduced phosphination of alkenes and alkynes. Depending on the structure and substitution of unsaturated substrate the oxydative phosphonation gives either phosphonates, phosphates or some products formed due to carbon-carbon bonds splitting. The different products may be explained by the different properties of intermediate radical-adducts:

$$\mathrm{RR'C{=}CH_2 + PCl_3 + O_2 \longrightarrow RR'\dot{C}{-}CH_2Cl \longrightarrow}$$

— (Chain propagation with PCl_3) ⟶ Phosphonates

— (Chain propagation with O_2) ⟶ Phosphates

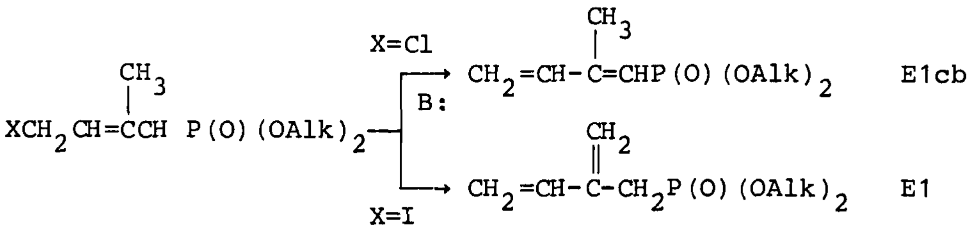
— (β-splitting) ⟶ Fragmentation

— (Recombination) ⟶ Clorides and isomers

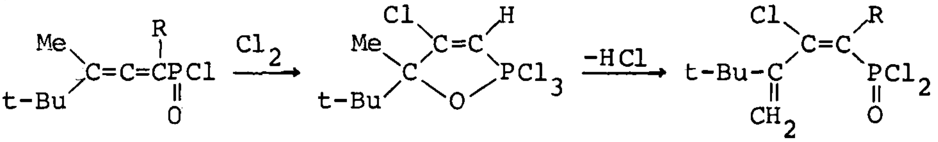
Photoinduced phosphination (PBr_3 addition) includes similar steps, but due to the absence of oxygen the final results are somewhat different. The main route is chain propagation with PBr_3 (quantum yields from 200 to 500); the side directions are recombination and isomer formation.

2. Construction of Unsaturated C-P Compounds.

Elimination of H-Hlg is a principal method of double bond construction in organophosphorus compounds. Under basic conditions E1cb process predominates, but introducing a readily leaving group sometimes initiates the E1 elimination:



Chlorination of allenic phosphonates resulted in the tetrachlorophospholene (3) formation. The latter slowly decomposes forming a conjugated diene (4). The HCl elimination step (E1) is fast and leaves double bond arrangement unchanged, so that the formation of strained dienes becomes possible.



3 4

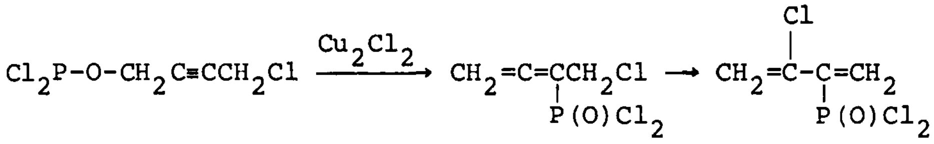
R: H, Ph, t-Bu, $ClCH_2$, $MeOCH_2$.

The electrophilic properties of alkyne phosphonates enable their application as dienophiles in Diels-Alder cycloaddition in diene - donor dienophile - acceptor system. Diphosphonoacetylenic esters and dichlorophosphonates are more active compared to alkyl- or arylacetylene phosphonic esters. Oxydation of diene adducts (by air) or H-Hlg elimination gives a number of orto-substituted benzene phosphonates.

3. Isomerizations of unsaturated phosphonates.

It is shown that prototropic isomerization of allyl phosphonic esters may be expanded on dichlorophosphonates which convert under the action of tertiary amines. The stereoselective isomerization of 3-chloro-2-propene 1-phosphonates to cis-3-chloro-2-propene is unexpected, and possibly determined by orientation of substrate and base molecules at the initial step of the process.

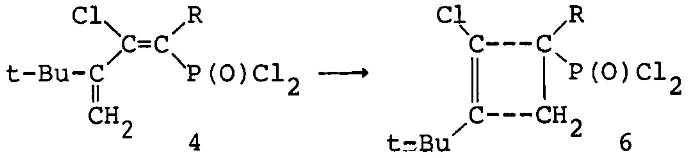
The action of Cu_2Cl_2 on 4-chloro-2-butynyldichlorophosphite initiates isomerization of the latter into conjugated diene (5). This reaction includes two step propargyl rearrangement:



$$Cl_2P\text{-}O\text{-}CH_2C{\equiv}CCH_2Cl \xrightarrow{Cu_2Cl_2} CH_2{=}C{=}\underset{P(O)Cl_2}{C}CH_2Cl \rightarrow CH_2{=}\overset{Cl}{C}\text{-}\underset{P(O)Cl_2}{C}{=}CH_2$$

5

The most significant result is 1,3-butadiene - cyclobutene isomerization of dichlorophosphonate (4). The conversion proceeds spontaneously under mild conditions due to decrease of steric strain.

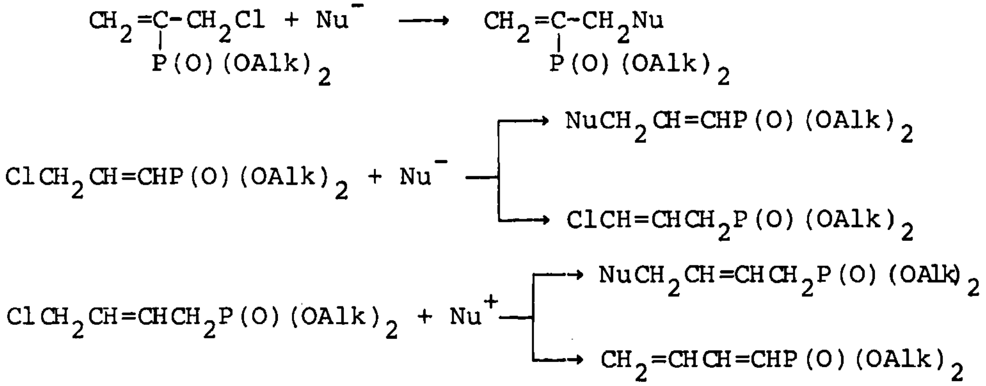


4 6

Similar reactions have been discussed as examples of four-electron electrocyclic conversion but there are only a few examples of their realization.

4. Substitution of Unsaturated Organophosphorus Compounds.

The nucleophilic substitution of halogene in haloallylphosphonates is an efficient method for molecular functionalisation. Meanwhile, if the reagent is basic, the alternative prototropic isomerization or H-Hlg elimination must be taken into account.



$$CH_2{=}\underset{P(O)(OAlk)_2}{C}\text{-}CH_2Cl + Nu^- \rightarrow CH_2{=}\underset{P(O)(OAlk)_2}{C}\text{-}CH_2Nu$$

$$ClCH_2CH{=}CHP(O)(OAlk)_2 + Nu^- \rightarrow NuCH_2CH{=}CHP(O)(OAlk)_2 \quad ; \quad \rightarrow ClCH{=}CHCH_2P(O)(OAlk)_2$$

$$ClCH_2CH{=}CHCH_2P(O)(OAlk)_2 + Nu^+ \rightarrow NuCH_2CH{=}CHCH_2P(O)(OAlk)_2 \quad ; \quad \rightarrow CH_2{=}CHCH{=}CHP(O)(OAlk)_2$$

Another route to functional derivatives is epoxydation of alkene phosphonates followed by oxyrane ring cleavage or isomerisation. The isomerisation of oxyrane phosphonates to phosphonoallylalcohols and chlorooxyrane phosphonates to phosphonochlorocarbonyl compounds was studied.