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Phosphorylated Allenes. Methods of Synthesis and Properties

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A systematic account is given of the literature data on the methods of synthesis of phosphorus-containing allenes. The unusual chemical behaviour of phosphorylallenes in their interaction with electrophilic addends is discussed and at the same time a new type of reaction, which leads to five-membered heterocycles containing a phosphorus atom directly in the ring, is considered. The review also deals with studies on nucleophilic addition to phosphorylallenes and
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I. INTRODUCTION

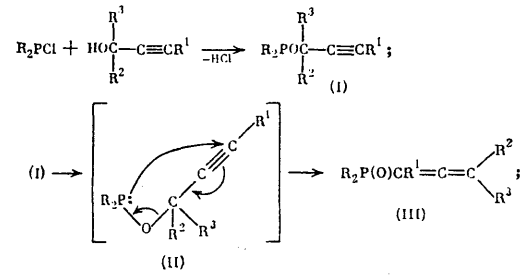
Considerable advances have been achieved in recent years in the synthesis and study of the chemical behaviour of phosphorylallenes. The enhanced reactivity of phosphorylallenes makes it possible to synthesise from them a wide variety of unsaturated organic open-chain and cyclic phosphorus compounds with functional-group substituents which are frequently difficult to obtain by other methods and which are likely to be useful as pesticides, medicinal drugs, monomers for the synthesis of plastics, etc. On the other hand, the characteristic features of the electronic structure of phosphorylallenes, in which the cumulene group with orthogonal π orbitals and different types of hybridisation of the carbon atoms (the sp^2 hybridisation of the extreme carbon atoms and the sp hybridisation of the middle carbon atoms) is combined with the electron-accepting phosphoryl group, is manifested in the physical and chemical properties of the compounds, which makes them convenient objects for the investigation of the interrelation between electronic structure, steric structure, and reactivity.

In a review of the chemistry of acetylenic and diene organophosphorus compounds (1967), mention was made of only seven allenylphosphonates;[1] since then, more than 200 phosphorus-containing allene derivatives have been synthesised. We thought it of interest and timely to survey the available information about the methods of synthesis of allene derivatives of tetracoordinate quinquevalent phosphorus. The present review also deals with certain physical characteristics of phosphorylallenes, their isomerisation, and their reactions with nucleophiles and electrophiles and derivatives of tervalent phosphorus. Studies on the 1,3-dipolar cycloaddition to phosphorylated allenes were considered earlier in other reviews.[2]

II. METHODS OF SYNTHESIS

1. The Acetylene–allene Rearrangement of Propargyl Phosphites and Phosphinites

The allene derivatives of tetracoordinate phosphorus have become available since the discovery of the acetylene–allene rearrangement of the propargyl esters of phosphorus and phosphinous acids, which are obtained from the chlorides of tervalent phosphorus acids and acetylenic alcohols in the presence of amines:[3-10]



(I) (II) (III)

R=CH_3, C_6H_5, AlkO, $HC{\equiv}CCH_2O$, $HC{\equiv}CCH(C_3H_7)O$, $HC{\equiv}CC(CH_3)_2O$, $R_3{=}{-}OCH_2\overset{CH_3}{\underset{|}{C}}HO{-}$;
R^1=H, CH_3; $R^2{=}R^3$=H, CH_3; R^2=H, $R^3{=}CH_3$;
$R^2{=}C_6H_5$, $R^3{=}CH_3$; $R^2+R^3{=}(CH_2)_4$, $(CH_2)_5$.

It has been suggested[3,10,11] that the rearrangement of the propargyl phosphite (phosphinite) (I) formed initially to the allenylphosphonate (III) takes place intramolecularly as an S_{n_i} reaction via the five-centre cyclic transition state (II) as a result of the energy gain associated with the change in the coordination of the phosphorus atom P(III) → P(IV). The isomerisation of (I) to (II) is also regarded as a variety of the Arbuzov reaction occurring with participation of phosphorohalidites.[12]

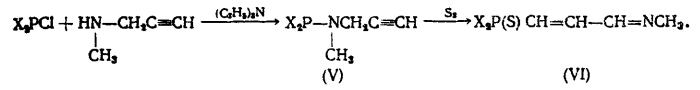
The high stereospecificity of the acetylene–allene rearrangement, which has been confirmed experimentally in relation to the interaction of the optically pure $R(+)$-2,2,6,6-tetramethylhept-4-yn-3-ol with phosphorus trichloride, leading after hydrolysis to the optically pure $R(-)$-1,3-di-(t-butyl)-propa-1,2-dienylphosphonic acid, enabled Macomber to assume the possibility that these reactions have the mechanism involving a concerted [3,2]sigmatropic shift.[13,14]

The allenyl phosphonate (III) formed can subsequently isomerise to the corresponding acetylenic derivative (IV):[6,7]

$$\underset{\text{(III)}}{R_2P(O)CH{=}C{=}CH_2} \rightarrow \underset{\text{(IV)}}{R_2P(O)C{\equiv}C{-}CH_3}.$$

The final result of the reaction is determined by its conditions, the method of treatment of the reaction mixture, and the presence of substituents in the propargyl group.[8,10] The formation of propargyl phosphites (I) in the first stage has been confirmed by their isolation in a pure state.[8,10,15,16] It is noteworthy that, whereas propargyl phosphites and phosphorothioites[17,18] readily rearrange to allene derivatives

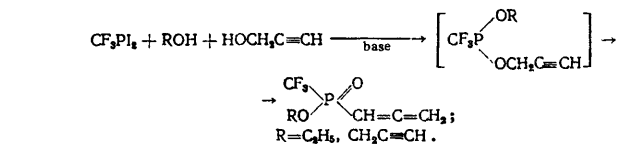
of tetracoordinate phosphorus, their nitrogen analogues (V) are more stable:[19]



(V) (VI)

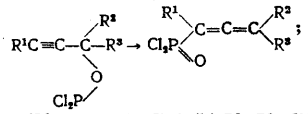
Only phosphines where X = C_2H_5 or C_6H_5 undergo the isomerisation (V) → (VI).

The rate of rearrangement of compound (I) to compound (III) depends to a large extent on the character of the substituents at the phosphorus atom and at the α-carbon atom in the propargyl group. Thus, the propargyl phosphinite (I), formed on interaction of chlorodiethylphosphine with propargyl alcohol, isomerises after several hours almost wholly with formation of an allenic phosphine oxide.[20] The propargyl esters of tervalent phosphorus acids, containing trifluoromethyl groups, also very readily isomerise to allene compounds:[21]



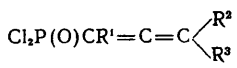
R=C_2H_5, $CH_2C{\equiv}CH$.

Like other phosphites containing the αα-disubstituted propargyl group, α-ethyl-α-methylpropargyl o-phenylene phosphite cannot be isolated in a pure state as a consequence of the rapid rearrangement of the corresponding phosphoryl allene.[22] The optimum condition for the rearrangement of propargyl phosphorodichloridite is ten day storage at room temperature.[16] Deuteriated propargyl phosphorodichloridite has been isomerised to the dichloride of α-deuterioallenylphosphonic acid by heating in benzene at 60–70° for 12 h.[23] Propargyl and α-methyl propargyl phosphorodichloridites isomerise to dichloroallenylphosphonates more slowly than αα-dimethylpropargyl phosphorodichloridite, whose acetylene–allene rearrangement to the chloride of 3-methylbuta-1,2-dienylphosphonic acid takes place especially readily.[12] The rate of rearrangement of acetylenic phosphorodichloridite to allenylphosphonate depends significantly on the substituents R^1, R^2, and R^3:



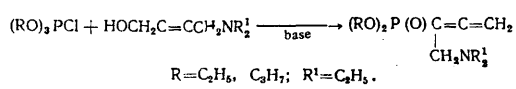
R^1=H, R^2R^3=$(CH_2)_4$ (a), $(CH_2)_5$ (b), R^2=R^3=CH_3 (c);
R^1=$(CH_3)_3C$, R^2=R^3=CH_3 (d), R^2=H, R^3=$(CH_3)_3C$ (e);
R^1=R^2=R^3=H (f).

It varies in the sequence a > b > c > d > e > f.[13,14] The dichlorides of allenylphosphonic acids formed under these conditions are convenient starting materials for the synthesis of the corresponding esters,[12,14] acid difluorides,[16] and acids.[13,14,24] Dimethyl(3-methylbuta-1,2-dienyl)phosphine oxide has been obtained from the dichloride of 3-methylbuta-1,2-dienylphosphonic acid and methylmagnesium iodide.[25,26] It is noteworthy that the dichlorides of the allenylphosphonic acids



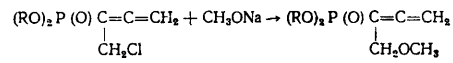
can also be obtained from propargyl alcohols and phosphorus trichloride using a vigorous stream of nitrogen to remove the hydrogen chloride formed from the reaction mixture.[14] The dichlorides of allenylphosphonic acids can also be obtained by refluxing the corresponding acetylenic alcohols in an excess of phosphorus trichloride or by treating the amides of alkal-1,2-dienylphosphonic acids with hydrogen chloride.[27]

When the appropriate substituents are introduced into acetylenic alcohols, it is possible to obtain phosphorylated allenes with alkyl and aryl substituents[28–32] and also with various functional groups at the C(1) and C(3) carbon atoms of the cumulene. Thus halogenopropargyl alcohols react with halogeno-derivatives of tervalent phosphorus acids to form α-halogenoallenylphosphonates[33,34] and the corresponding phosphine oxides.[35,36] The products of the interaction of dialkyl phosphorochloridites with 4-*NN*-dialkylaminobut-2-yn-1-ols undergo thermal isomerisation with formation of dialkylaminomethyl-substituted propa-1,2-dienylphosphonates:[37]



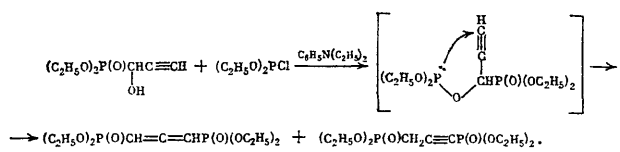
R=C_2H_5, C_3H_7; R^1=C_2H_5.

The dialkyl esters of 1-chlorobuta-2,3-dien-2-ylphosphonic acids[38] are unstable and have not been isolated in a pure state. Their formation has not been established either spectroscopically or from their chemical reactions. When sodium methoxide is introduced into the reaction mixture, chlorine is substituted by the alkoxy-group with formation of esters of 1-methoxybuta-2,3-dien-2-ylphosphonic acid:[39]



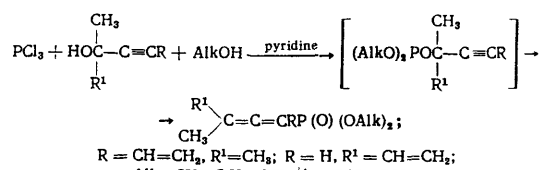
The latter have also been obtained by specific synthesis—the acetylene–allene rearrangement of the products of the interaction of 4-methoxybut-2-yn-1-ol with dialkyl phosphorochloridites.[35] The acetylene–allene isomerisation of the corresponding acetylenic phosphites, formed when the monomethyl ethers of acetylenic glycols are treated with phosphorus trichloride in the presence of pyridine, yielded the dichlorides of 1-methoxyalka-2,3-dien-2-ylphosphonic acids.[40] Dialkyl(1-methoxyalka-2,3-dien-2-yl)phosphine oxides have been synthesised by the reaction of the dichlorides of 1-methoxyalka-2,3-dien-2-ylphosphonic acids with alkylmagnesium halides.[40]

The interaction of 1-hydroxyprop-2-ynylphosphonic ester with diethyl phosphorochloridite afforded a mixture of allenic and acetylenic diphosphonates:[41]



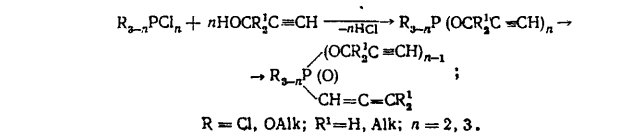
The esters of allenylphosphinothioic acids have been obtained by the isomerisation of the products of the interaction of dialkyl phosphorochloridites with acetylenethiols.[17,18]

The dialkyl esters of 1- and 3-vinylallenylphosphonic acids are formed when vinylacetylenic alcohols are treated with phosphorus trichloride and this is followed by the acetylene–allene isomerisation of the intermediate mixed phosphites;[32,33]

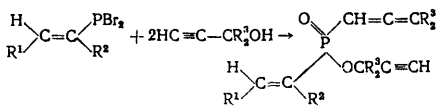


R = $CH{=}CH_2$, R^1=CH_3; R = H, R^1 = $CH{=}CH_2$;
Alk=CH_3, C_2H_5, C_3H_7, iso-C_3H_7, C_4H_9.

By substituting the halogen atoms in the corresponding halogeno-derivatives of tervalent phosphorus by acetylenic alcohol residues, it is possible to synthesise highly unsaturated phosphorylallenes:[3,4,42]

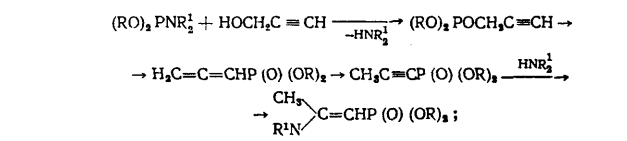


The reactions of the dibromides of alkenylphosphonous acids with acetylenic alcohols take place with rapid acetylene–allene isomerisation of the products, which leads to the monoalkynyl esters of alkenyl(allenyl)phosphinic acids:[43,44]

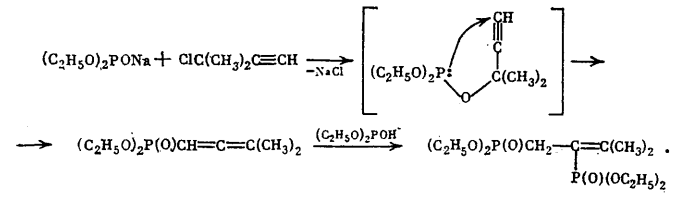


Alkyl allenylphosphonochloridates[44] and alkyl diethylaminoallenylphosphonates[45] have been obtained from propargyl alcohols and the corresponding tervalent phosphorus derivatives.

The alcoholysis of phosphoramidites by propargyl alcohol at 80–100 °C leads to the formation of propargyl phosphites, which immediately isomerise to allenylphosphonates and further to propynylphosphonates.[45] However, the reaction does not stop at this stage: the dialkylamine evolved adds to the triple bond of the propynylphosphonate:

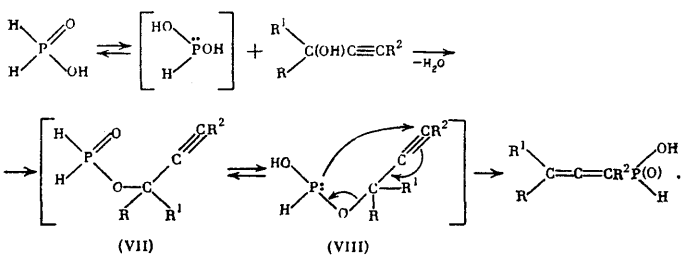


The reaction of sodium diethyl phosphite with 2-chloro-2-methylbut-3-yne in ethereal solution yielded 1-diethylphosphono-3-methylbuta-1,2-diene and the product of the addition of diethylphosphorous acid to the latter:[46]



The allenylphosphonate, formed analogously in the reaction of sodium diethyl phosphite with propargyl bromide, isomerises to propynylphosphonate.[47]

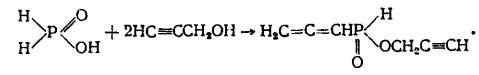
A large series of allenylphosphorous acids containing an active P–H bond have been synthesised by esterifying hypophosphorous acid with acetylenic alcohols:[48–57]



(VII) (VIII)

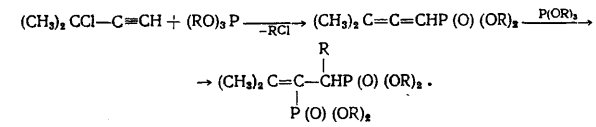
Despite the fact that the propargyl phosphite (VII) formed in the first stage contains a tetracoordinate phosphorus atom, the presence of two P–H bonds promotes the shift of the tautomeric equilibrium towards the tricoordinate form (VIII) to a larger extent than in the case of phosphite esters.[56] The high nucleophilicity of phosphorus in the intermediate (VIII) is responsible for the possibility of the acetylene–allene rearrangement.

By altering the reactant ratio, it is possible to obtain the propargyl esters of propa-1,2-dienylphosphonous acid:[52]

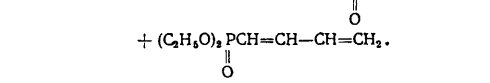


2. Other Methods of Synthesis of Phosphoryl Allenes

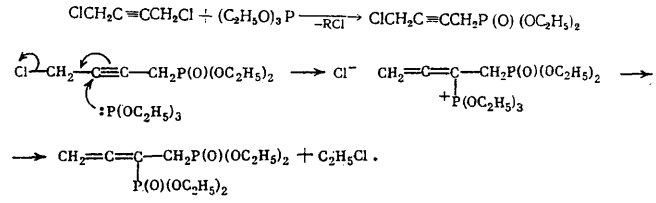
In a study of the Arbuzov reaction involving trialkyl phosphites and 2-chloro-2-methylbut-3-yne, the esters of 3-methylbuta-1,2-dienylphosphonic acid were obtained for the first time.[58] The reaction did not stop at this stage and a second molecule of the trialkyl phosphite added to the allenylphosphonate formed:



A mixture of buta-2,3-dienyl- and buta-1,3-dienyl-phosphonates is formed when triethyl phosphite reacts with 1-chlorobuta-2,3-diene:[59]



When 1,4-dichlorobut-2-yne is used, an asymmetric diphosphonate with an allene structure, namely the tetraethyl ester of buta-2,3-dien-1,2-ylenediphosphonic acid, is formed in addition to 4-chlorobut-2-ynylphosphonate:[60]



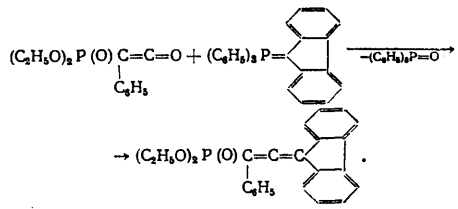
The formation of the allenediphosphonate is due to the reduced reactivity of the propargyl chloride group in 4-chlorobut-2-ynylphosphonate compared with the corresponding bromide in the Arbuzov reaction (in the latter case but-2-yn-1,4-ylenediphosphonate was obtained).

The reaction of propargyl bromide with trialkyl phosphite is of the type of Arbuzov rearrangement, being accompanied by the prototropic isomerisation of allenylphosphonate to propynylphosphonate.[61,62]

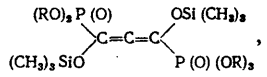
Diethyl allenylphosphonate has been obtained by the dehydrobromination of 2-bromo-1-diethylphosphonoprop-2-ene with the aid of a Grignard reagent.[63,64] The use of stronger bases (sodium alkoxide or hydride) in this reaction leads to the formation of propynylphosphonate.

C(1)- and C(3)-substituted *OO*-dimethylphosphonoallenes have been obtained in low yields in the photolysis of phosphorylvinylcarbenes.[65]

Trisubstituted phosphorylated allenes can be obtained from phosphorylketones and phosphorus ylides: [66]



A method of synthesis of 1,3-bis(dialkylphosphono)-1,3-bis-trimethylsiloxy)allenes



where R is ethyl or propyl, by the reaction of dialkyl trimethylsilyl phosphite with carbon suboxide at −30 to −70 °C, [67] has been proposed.

III. THE PROPERTIES OF PHOSPHORYLATED ALLENES

1. Structure and Physical Characteristics

Quantum-chemical calculations by the CNDO/2 method in terms of the *spd* basis set have shown that the electron density at the C(3) carbon atom increases significantly on passing from 3-alkyl-substituted to unsubstituted allenylphosphonates and -phosphonites on subsequent redistribution of the effective charges (Table 1). [68]

Table 1. Results of calculations for phosphorus-containing allenes $R^1R^2P(O)C^1H=C^2=C^3XY$ by the CNDO/2 method in terms of the *spd* basis set. [68]

R^1	R^2	X	Y	Atomic charges, a.u.				
				C(1)	C(2)	C(3)	P	=O
Cl	Cl	H	H	−0.138	0.159	−0.122	0.257	−0.252
Cl	Cl	H	CH_3	−0.139	0.134	−0.050	0.254	−0.258
Cl	Cl	CH_3	CH_3	−0.137	0.112	−0.002	0.249	−0.258
F	F	H	H	−0.162	0.160	−0.117	0 602	−0.293
CH_3O	CH_3O	H	H	−0.155	0.143	−0.123	0.453	−0.329
CH_3O	CH_3O	H	CH_3	−0.157	0.120	−0.053	0.443	−0.332
CH_3O	CH_3O	CH_3	CH_3	−0.155	0.102	−0.007	0.442	−0.334
CH_3	CH_3	CH_3	CH_3	−0.161	0.112	−0.016	0.453	−0.335
HO	HO	CH_3	CH_3	−0.165	0.114	−0.006	0.255	−0.315
HO	H	H	H	−0.166	0.173	−0.135	0.401	−0.319
HO	H	CH_3	CH_3	−0.163	0.125	−0.008	0.39	−0.325

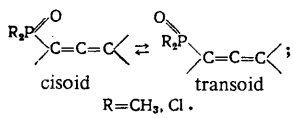
The ^{13}C chemical shift in the ^{13}C NMR spectra of phosphorylated allenes reflect the general characteristics of their structure. The signal of the *sp*-hybidised C(2) carbon atom is in the low field region (211–218 p.p.m.), while the C(1) and C(3) nuclei give rise to signals characteristic of the sp^2-hybidised atom (75–103 p.p.m.) [68] (Table 2).

The ^1H and ^{31}P NMR spectra of phosphorylated allenes have been described fairly fully in the literature [14,20,25,27,29,30,32,69,70], etc.). The chemical shift due to the phosphorus atom in the ^{31}P NMR spectra of allenylphosphonates is manifested by a signal in the range 15–20 p.p.m., shifting to the region 25–30 p.p.m. for allenylphosphine oxide and the dichlorides of allenylphosphonic acids.

Table 2. Parameters of the ^{13}C NMR spectra of allenic phosphonates and phosphinites $R^1R^2P(O)C^1R^3=C^2=C^3XY$. [68]

R^1	R^2	R^3	X	Y	Chemical shifts δ_C, p.p.m.				Spin-spin interaction constants J_{PC}, Hz			
					C(1)	C(2)	C(3)	CH_3	C(1)	C(2)	C(3)	CH_3
Cl	Cl	H	H	H	89.7	212.1	79.3	—	164.1	2.8	21.5	—
F	F	H	H	H	80.9	217.3	78.3	—	222.3	0	18.8	—
C_2H_5O	C_2H_5O	H	H	H	79.8	218.6	75.8	—	197.6	0	15.7	—
C_2H_5O	C_2H_5O	CH_3	H	H	88.7	216.0	75.7	14.2	190.1	6.4	15.4	5.0
CH_3O	CH_3O	H	H	H	77.4	215.5	96.8	19.1	195.8	3.4	16.4	6.9
Cl	Cl	H	CH_3	CH_3	89.4	209.3	103.8	18.8	162.0	4.3	24.2	9.5
CH_3	CH_3	H	CH_3	CH_3	85.4	207.8	96.5	16.1	100.4	0	13.4	6.1
HO	H	H	H	H	92.4	217.5	85.9	—	132.5	0	15.0	—
HO	H	H	CH_3	CH_3	80.8	211.3	99.8	—	193.0	0	17.0	—

The band due to the antisymmetric vibrations of the C=C=C group in the region of 1950 cm^{-1} in the IR spectra of phosphorylallenes was found to be a doublet, [16,20,71] which can be explained by the conformational isomerism arising as a consequence of the rotation relative to the $P-C_{sp^2}$ bond. [71] Using the set of IR and Raman spectroscopic data, dipole moments, and Kerr effect data, it has been shown that, in the liquid state and in solutions of dimethyl(3-methylbuta-1,2-dienyl)phosphine oxide and the chlorides of 3-methylbuta-1,2-dienylphosphonic and propdienylphosphonic acids, there is a conformations equilibrium between the cisoid and transoid forms, somewhat displaced towards the latter: [26]



R=CH_3, Cl.

The study of the molecular geometry for a series of allenyldiphenylphosphine oxides by ^1H NMR [29,72–76] has shown that a diamagnetic anisotropy has arisen under the influence of the aromatic nuclei attached to the phosphorus atom. Conformational analysis of these systems relative to the σ-bond between the terminal C(3) carbon atom of the phosphorylated cumulene and the substituent at this atom indicates a structure with the $C_{sp^2}-C_{sp^3}$ bond eclipsed by the allene system. Whether or not this orientation is preferred depends on the substituents at the C_{sp^3} carbon atom and varies in the sequence $CH_3 \gg C_6H_5 > H$.

2. Isomerisation

The isolation of esters of the 3,3-unsubstituted allenylphosphonic acid frequently presents considerable difficulties owing to the ready isomerisation to methylacetylenic phosphonates. [8] The prototropic conversion of allenylphosphonate into propynylphosphonate by treatment with propargyl phosphite, which plays the role of a basic catalyst, or in the presence of amines, alkoxides, and phosphites is accompanied by an increase of temperature and takes place quantitatively. The isomerisation of allenyldiethylphosphine oxide to the corresponding acetylenic derivative is slower compared with

allenylphosphonate, which is apparently associated with the weaker electron-accepting properties of the diethylphosphine oxide group.[20]

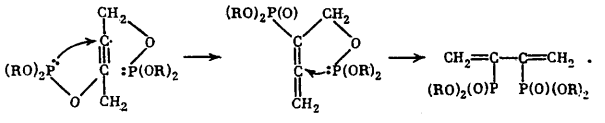
Allenylphosphonic acid dichloride and alkyl allenylphosphonochloridate do not undergo the prototropic transformation into acetylenic derivatives on heating for several hous at 100–150 °C.[34]

3-Monosubstituted allenylphosphonates are more resistant to prototropic isomerisation compared with propadienylphosphonates, which agrees with the charge distribution in phosphorylallenes[68] (Table 1). When diethylphosphonobuta-1,2-diene is heated in the presence of sodium ethoxide at 100 °C for 1.5 h, it isomerises to only a slight extent[77] and an equilibrium mixture is formed after 5 h at 160–180 °C:[78]

$$\underset{70\%}{CH_3C{\equiv}CCH_2P(O)(OC_2H_5)_2} \rightleftarrows \underset{20\%}{CH_3CH{=}C{=}CHP(O)(OC_2H_5)_2} \rightleftarrows \underset{10\%}{CH_2{=}C{=}CHCH_2P(O)(OC_2H_5)_2}.$$

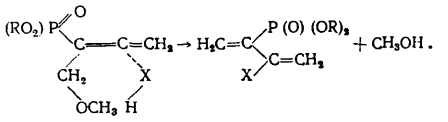
3,3-Disubstituted allenylphosphonates and allenylphosphine oxides are thermodynamically stable and do not isomerise to acetylenic derivatives.[8,78]

The allene–diene isomerisation is observed in the thermal rearrangement of diphosphites with a βγ-acetylenic bond in the common ester residue:[9]



Phosphonoprenes have been obtained by allene–diene isomerisation on distillation of relatively unstable esters of 1-chlorobuta-2,3-dien-2-ylphosphonic and 1-chloro-4-methylpenta-2,3-dien-2-ylphosphonic acids.[38,79]

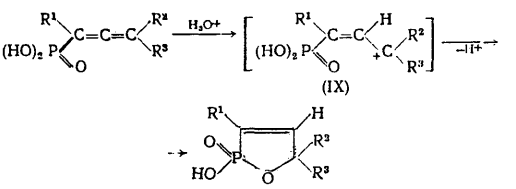
When dialkyl 1-alkoxybuta-2,3-dien-2-ylphosphonates are treated with hydrogen halides, the allene–diene isomerisation takes place with formation of esters of 3-halogenobuta-1,3-diene-2-ylphosphonic acid:[80,81]



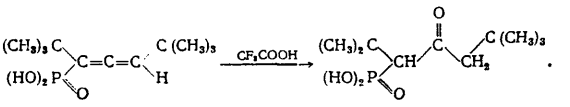
3. Electrophilic Addition

(a) Interaction of Phosphorylallenes with Proton-Donating Reagents

The reactions involving electrophilic addition to phosphorylallenes, in the course of the study of which a new reaction has been discovered, namely heterocyclisation, aroused most interest in recent years. In the study of the reactions of propargyl alcohols with phosphorus tribromide in 1971, it was observed that, when the HBr evolved is not bound by a base, then crystals of 2-bromo-3,5-di-t-butyl-2-oxo-1,2-oxa-3-phospholen are formed from 2,2,6,6-tetramethylhex-4-yn-3-ol.[82] Subsequent investigations demonstrated that the oxaphospholen is formed from phosphonoallene on treatment with proton donors.[13,14] The ease of the acid-catalysed cyclisation of allenylphosphonic acids depends to a large extent on R^2 and R^3 and to a lesser extent on R^1:



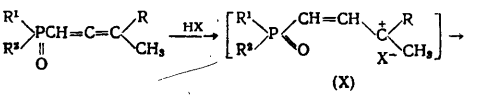
If $R^2 = R^3 = H$, then cyclisation is fully suppressed.[13] A necessary condition for cyclisation is the presence of alkyl substituents at the terminal carbon atom of phosphorylallene. The influence of substituents on the rate of cyclisation has been attributed[13] to the stability of the intermediate carbenium ion (IX), which arises in the stepwise protonation of the double bond; subsequent nucleophilic attack by the phosphoryl oxygen on the carbenium centre leads to the closure of the five-membered ring. Protophilic cyclisation proceeds as a rule regioselectively with attack by the proton on the central atom of the allene system. It might have been thought that not only Brønsted acids but also other electrophiles would promote the cyclisation of allenylphosphonic acids to the more stable oxaphospholen derivatives.[13] However, the attempt to cyclise 1,3-di-t-butylallenylphosphonic acid in trifluoroacetic acid leads to unexpected deviations,[83] which can be explained, according to the authors, by electophilic attack not on the central but on the terminal carbon atom of the allene system:

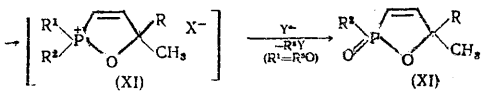


The cuases of the terminal attack by trifluoroacetic acid are not discussed in the above communication. They are most probably associated with the steric hindrance to the protonation of the central *sp*-hybridised carbon atom.

The interaction of allenylphosphonic acids with peracids leads to the formation of a mixture of products containing 4-oxo-1,2-oxaphospholan.[84]

The reactions of proton-donating electrophiles with allenylphosphonic acid esters have been fairly fully investigated.[85–89] The hydrochlorination of the dialkyl esters of 3-alkylalka-1,2-dienylphosphonic acids in polar solvents[85,86] entails cyclisation with formation of 1,2-oxaphospholens, as in the case of the allenylphosphonic acids themselves.[13,14] A general mechanism has been proposed for the cyclisation of 3,3-disubstituted allenylphosphonates in acid media, including the protonation of the central atom of the allene.[87] Subsequent attack by the internal nucleophile on the carbenium ion centre formed in the intermediate (X) leads to the cyclic quasi-phosphonium intermediate (XI) which in the case of alkoxy-substituents at the phosphorus atom is stabilised with elimination of an alkyl halide, analogously to the second stage of the Arbuzov reaction. The formation of the quasi-phosphonium intermediate (XI) in the protophilic cyclisation of phosphorylated allenes has been confirmed by the formation, in a pure state, of the crystalline quasi-phosphonium salt (XI) on hydrochlorination of allenylphosphine oxide[88] for which the occurrence of a second stage of the Arbuzov reaction is impossible:



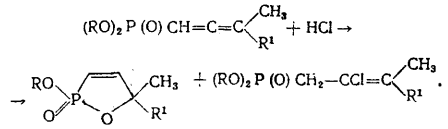


(XI) (XI)

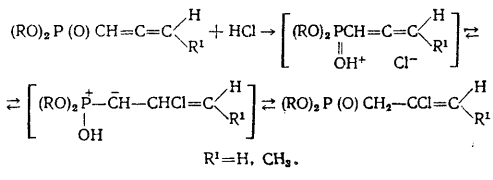
R=R¹=R²=CH₃; R=CH₃, R¹=CH₃O, R²=C₆H₅, CH₃O;
R=CH₃, R¹=R²=iso-C₃H₇; R=C₂H₅, R¹=R²=CH₃O;
X=Cl⁻, HSO_4^-, CF_3COO^-;
Y=Cl⁻, HSO_4^-, CF_3COO^-, HO⁻, H₂O.

Kinetic study of the reactions of phosphorylallenes with aqueous solutions of sulphuric acid and anhydrous trifluoroacetic acid has shown that the protonation of the multiple bond is the slowest stage of the process considered.[87] The dependence of the rate of reaction on the acidity function of the medium and on the activation parameters indicates an appreciable degree of order in the transition state of the reaction. The acid-promoted cyclisation is an electrophilic addition reaction involving the proton and the substrate in the rate-determining stage. The protonation of the phosphoryl group slows down the reaction as a consequence of the destabilisation of the carbenium ion.

When non-polar solvents are used, products of the addition to the 1,2-double bond in allenylphosphonates are formed in the same amounts as the oxaphospholen derivatives. The yield of the 1,2-adducts reaches 80% when dimethyl sulphoxide is introduced into the reaction mixture as the aprotic ionising additive:[87]



The hydrochlorination of esters of unsubstituted allenylphosphonic acids or the acids monoalkyl-substituted at the terminal carbon atom leads to a complex mixture of open-structure compounds regardless of the polarity of the medium with the preferential formation of the products of addition to the 1,2-double bond of the allene system.[86] The authors postulate that the formation of 1,2-adducts is associated with the difficulty of stabilising the carbenium ion of type (X), which results in the competing reaction involving the nucleophilic addition of HCl:



R¹=H, CH₃.

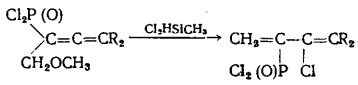
In the hydrochlorination of the dichloride of 3-methylbuta-1,2-dienylphosphonic acid, an oxaphospholen with a pentacoordinate phosphorus atom is formed slowly.[14] In the presence of aprotic ionising additives, the addition of hydrogen chloride to the dihalides of allenyl phosphonic acids leads to the formation of 1,2-adducts[89] and the introduction of alkyl substituents at the C(3) carbon atom of the cumulene system retards the reaction under these conditions. In the hydrochlorination of the dichloride of unsubstituted allenylphosphonic acid, a mixture of products of addition to the 1,2- and 2,3-double bond has been obtained:

$$Cl_2P(O)CH{=}C{=}CH_2 + HCl \rightarrow Cl_2P(O)CH_2CCl{=}CH_2 + Cl_2P(O)CH{=}CCl{-}CH_3.$$
Z and *E*

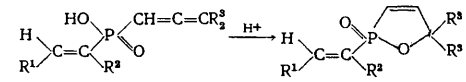
When dichloromethylsilane is used as the hydrochlorinating agent, hydrogen chloride adds to the 1,2- and 2,3-double bonds of the dichlorides of allenylphosphonic acids and a mixture of structural isomers is formed:[40]

$$Cl_2P(O)CH{=}C{=}CR_2 \xrightarrow{Cl_2HSiCH_3} Cl_2P(O)CH_2CCl{=}CR_2 + Cl_2P(O)CH{=}CCl{-}CHR_2.$$

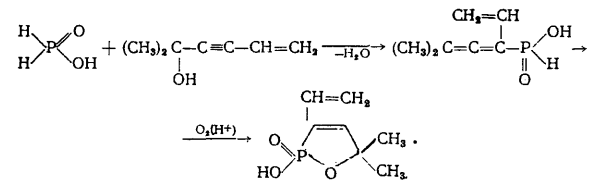
The dichlorides of 1-methoxyalka-2,3-dien-2-ylphosphonic acids react with dichloromethylsilane with the exclusive formation of the dichlorides of 3-chloroalka-1,3-dien-2-ylphosphonic acids:[40]



Highly unsaturated phosphorylallenes are converted into oxaphospholens under severe conditions (>100 °C) in the presence of inorganic acids:[44]

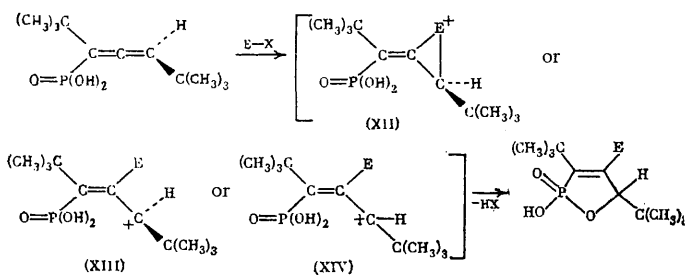


After prolonged heating of a mixture of hypophosphorous acid and Nazarov's carbinol, heterocyclisation takes place with oxidation of the P–H bond by atmospheric oxygen and the formation of 1,2-oxaphospholen:[54]



(b) The Interaction of Phosphorylated Allenes with Electrophiles Which Do not Contain a Proton

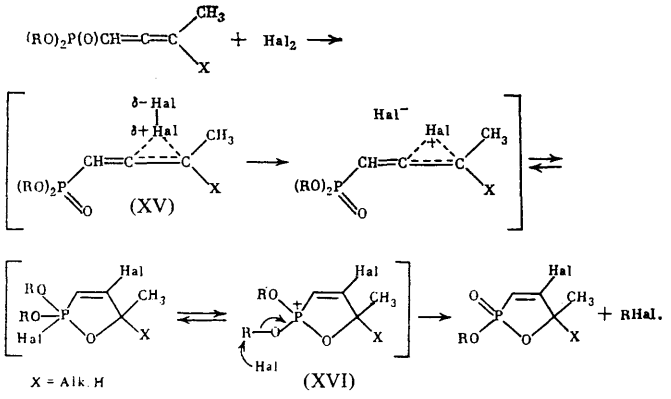
The hypothesis that phosphorylallenes are able to cyclise to 1,2-oxa-2-phospholens on treatment with not only acids but also other electrophiles[13] has been confirmed in the study of their reactions with bromine and mercury acetate. It was found that these electrophiles act more effectively than the proton-donating electrophiles. Thus 1,3-di-t-butylpropa-1,2-dienylphosphonic acid, which does not form oxaphospholens on treatment with Brønsted acids, readily cyclises on interaction with bromine or mercury acetate.[13] The stereospecificity of the interaction of electrophiles with optically active allenylphosphonic acids (81% for mercury acetate and 41% for bromine) is determined by the ability of the nucleophilic phosphoryl oxygen atom to stabilise the carbonium ion formed, which prevents racemisation. The regioselectivity of the reaction with attack by the electrophile on the central carbon atom can be accounted for by the same cause.



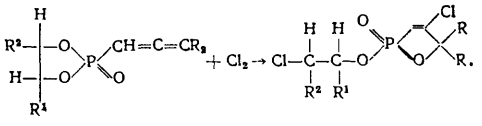
(XIII) (XIV)

An intermediate in this reaction may be either the cyclic ion (XII) or the non-planar carbenium ion (XIII), which are responsible for the retention of configuration. The slight racemisation of the optically active compound may be caused by the formation of the intermediate planar allyl cation (XIV).

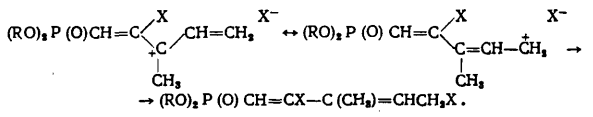
The formation of 1,2-oxa-3-phospholens is observed on interaction of bromine with allenylphosphonic acids.[90] Cyclisation takes place also when esters of 3-mono- and 3,3-di-substituted allenylphosphonic and allenylphosphinic acid are treated with halogens.[90-93] The authors[91] suggest that the π-complex or halogenium ion (XV) arising in the initial stage is converted into the cyclic quasi-phosphonium complex (XVI) as a result of the involvement of the phosphoryl oxygen:



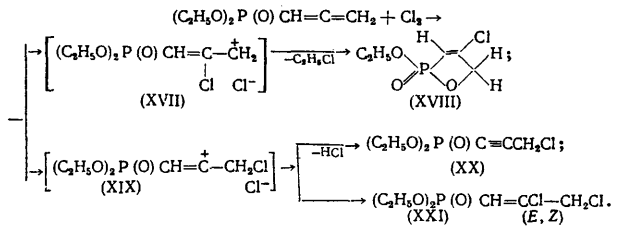
The authors assume that the pentacovalent structure is partly ionised and that the subsequent dissociation of the ion pair produced leads to equilibrium between tetracoordinate and pentacoordinate structures. In the case of alkoxy-groups with smaller moieties both structures are unstable and the system is stabilised by the concluding stage of the Arbuzov reaction—the elimination of the alkyl halide with formation of oxaphospholen. The rate of formation of oxaphospholens depends on the nature of the halogen and diminishes in the sequence ClI > BrI > I_2.[94] It is noteworthy that, in the interaction of allene derivatives of 1,2,3-dioxaphospholans with chlorine, the dioxaphospholan ring is cleaved and β-chloroalkoxy-1,2-oxa-3-phospholens are formed without the elimination of the alkyl chloride:[95]



The introduction of the vinyl substituent in the 1- or 3-position in buta-1,2-dienylphosphonate does not alter the mode of interaction with halogens despite the appearance of a new reaction centre in the molecule: 3- or 5-vinyl-substituted 4-halogeno-1,2-oxa-3-phospholens are formed.[96,97] The esters of penta-1,2,4-trienylphosphonic acid afford on halogenation a small amount of 1,4-adducts together with oxaphospholens. This mode of addition has been explained by the authors by the possibility of the resonance stabilisation of the allyl cation:[97]

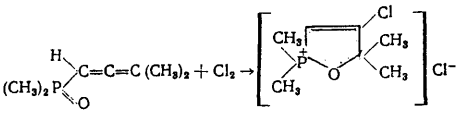


When the diethyl ester of propadienylphosphonic acid is chlorinated, a complex mixture of products is formed[92] in which it was possible to detect by NMR the oxaphospholen (XVIII), the ester of 3-chloroprop-1-ynylphosphonic acid (XX), and the ester of 2,3-dichloroprop-1-enylphosphonic acid (XXI) (the *E*- and *Z*-isomers) in the proportions (XVIII) : (XX) : (XXI) = 2 : 3 : 1. The mixture also contains a small amount of diethyl *E*-2-chloropropenylphosphonate. The formation of the ion (XIX) as an intermediate, together with the ion (XVII), leads to open-chain compounds:

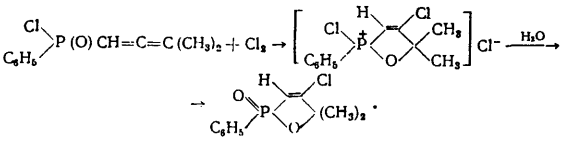


The introduction of electron-donating alkyl groups entails a significant difference between the energetic stabilities of the ions of the two types, which virtually rules out the formation of the intermediate (XIX).[91]

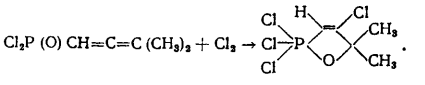
In the chlorination of buta-1,2-dienylphosphine oxides, the second stage of the Arbuzov reaction is impossible, as a result of which stable quasi-phosphonium salts are formed:[98]



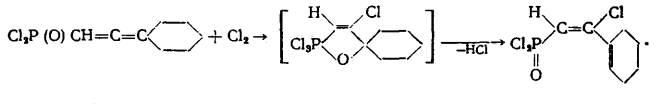
However, the chlorination of diphenylalka-1,2-dienylphosphine oxides, substituted and unsubstituted at the terminal carbon atom, leads to adducts with an open structure. The authors explained this mode of reaction by steric hindrance arising, owing the the presence of the bulky phenyl groups, in the overlap of the *p*-orbitals of the phosphoryl oxygen with the *p* orbital of the carbenium ion formed in the intermediate stage. The replacement of one phenyl group by the more electron-accepting chlorine atom leads to the formation of a ring:[98]



Cyclic phosphoranes—oxaphospholens with a pentacoordinate phosphorus atom—are formed when the chlorides of alka-1,2-dienylphosphonic acids are chlorinated:[99-102]

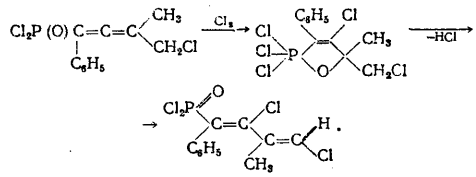


In the interaction of bromine the formation of a phosphorane cannot be observed possibly as a consequence of the more polar structure, compared with that of the phosphorane, of the bromo-derivatives of phosphorus.[100] On heating or storage, compounds of the phosphorane type split off HCl and are converted into 1,3-diene derivatives:[100-102]



The chlorination of the dichlorides of 1,3,3-trisubstituted allenylphosphonic acids also affords products with the

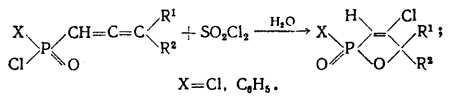
1,3-diene structure,[40,103–105] for example:



The chlorination of the dichloride of 1-t-butyl-4-chloro-3-methylbuta-1,2-dien-1-ylphosphonic acid leads to the formation of a stable quasi-phosphonium salt and the product of addition to the 2,3-double bond.[105] The stabilisation of the phosphonium salt is achieved as a consequence of the electronic and steric effects of the t-butyl group.

The interaction of chlorine with the dichloride of propyldienylphosphonic acid leads mainly to the formation of products of addition to the 2,3-double bond with an open structure.[92]

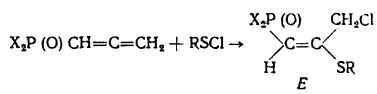
The interaction of the chlorides of 3-mono- and 3,3-disubstituted allenylphosphonic acids with sulphuryl chloride entails the formation of 1,2-oxaphospholens:[98,106]



X=Cl, C_6H_5.

A complex mixture of products of addition to one and two double bonds is formed in the chlorination of the dichloride of allenylphosphonic acid by sulphuryl chloride.[106]

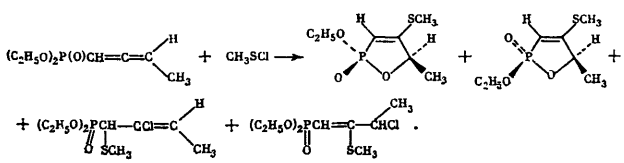
The addition of arene- and alkane-sulphenyl chlorides to the esters and dichloride of 3,3-unsubstituted allenylsulphonic acid and also to allenyldiphenylphosphine oxide takes place regioselectively and stereospecifically. Attack on the 2,3-double bonds of the cumulene takes place in the sterically more favourable *anti*-position relative to the bulky phosphoryl group located in the plane of the reacting double bond, with formation of mainly the *E*-isomer:[107–110]



X=AlkO, Cl, C_6H_5; R=C_6H_5, *p*-$CH_3C_6H_4$, Alk.

Similarly, selenyl chlorides form 2,3-adducts on interaction with allenylphosphonates but the *Z*-isomer predominates in the case of benzeneselenyl chloride.[111]

The introduction of alkyl substituents in the 3-position in phosphorylallene alters the mode of reaction. The ester of 3-monosubstituted allenylphosphonic acid reacts with arene- and methanesulphenyl chlorides to form diastereoisomeric oxaphospholens and also products of addition to the 1,2- and 2,3-double bonds of the cumulene in proportions of 4:1:1:1:[110]

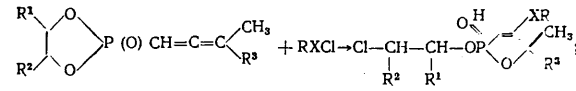


The orientation of the methylthio-group and of the chlorine atom in the 1,2-adduct has been confirmed by comparing the experimental chemical shifts of the proton at the olefinic carbon with the theoretical calculations. The diastereoisomeric oxaphospholens and products of addition to the 2,3-double bonds were not detected in the study of Angelov et al.[112] and a structure with the opposite positions of the alkylthio-group and the chlorine atom, compared with that found by Khusainova et al.,[110] was attributed to the product of addition to the 1,2-double bond.

Methaneselenyl chloride reacts with 3-monosubstituted allenylphosphonate to form an adduct at the 2,3-double bond and a small amount of a cyclic product (10%), while benzeneselenyl chloride affords exclusively the oxaphospholen.[111]

The esters of 3,3-disubstituted allenylphosphonic acids interact with alkane-, arene-,[107,113,114] and phosphonosulphenyl chlorides[110] and also with their selenium analogues[115,116] to form cyclic 4-organylthio(seleno)-1,2-oxa-3-phospholens with elimination of alkyl halides.

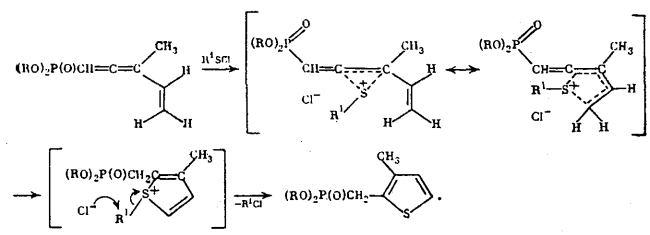
The reactions of sulphenyl and selenyl chlorides with 2-(alka-1,2-dienyl)-1,3,2-dioxaphospholan 2-oxides take place with cleavage of the dioxaphospholan ring and the formation of 1,2-oxaphospholens:[117]



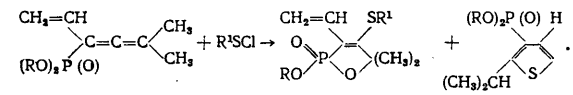
X = S or Se; R=CH_3, iso-C_3H_7; R^1, R^2, R^3=Alk.

Very small amounts of 1,2-adducts of methanesulphenyl chloride with 3-alkyl-3-methylallenylphosphonates have also been detected by column chromatography in the form of a mixture of *E*- and *Z*-isomers;[118] selenyl chloride interacts exclusively via the heterocyclisation mechanism.

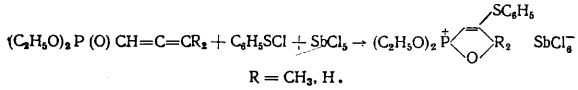
The introduction of the vinyl group into 3-methylpropa-1,2-dienylphosphonate at the C(3) carbon atom leads to the formation of phosphonylated thiophens in the reactions with alkanesulphenyl chlorides:[119]



1,3,3-Trisubstituted allenylphosphonates react with alkanesulphenyl chlorides to form 4-alkylthio-1,2-oxa-3-phospholens.[112] However, when the substituent at the C(1) carbon atom of the allene is a phenyl group, then linear products of the 2,3-addition of alkanesulphenyl chloride are formed together with oxaphospholens.[112] When the vinyl substituent is introduced into the geminal position relative to the phosphoryl group, the reaction of 1,3,3-trisubstituted phosphonoallene with alkanesulphenyl chlorides leads to the formation of a mixture of two heterocycles—thiophen and oxaphospholen:[120]

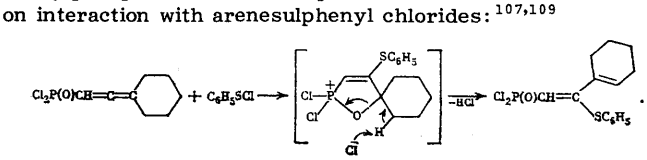


Stable quasi-phosphonium salts have been obtained by the reaction of 3,3-disubstituted and unsubstituted allenylphosphonates with benzenesulphenyl chloride in the presence of $SbCl_5$:[121]



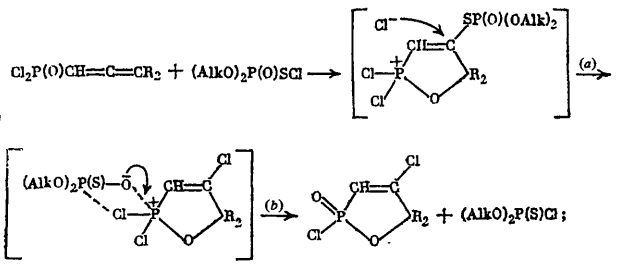
R = CH_3, H.

In contrast to esters, the dichlorides of 3,3-disubstituted allenylphosphonic acids form products with a diene structure on interaction with arenesulphenyl chlorides:[107,109]



Areneselenyl chlorides react with the dichloride of cyclohexylidenevinylphosphonic acid in the presence of SO_2 to form five-membered heterocycles.[116]

Phosphonosulphenyl chlorides react with the dichloride of 3,3-disubstituted allenylphosphonic acids to form 2,4-dichloro-oxaphospholen and the chlorides of the corresponding phosphorothioic acids, apparently via the following mechanism:[110]



R=CH_3, R_2=$(CH_2)_5$; Alk=CH_3, iso-C_3H_7.

Nucleophilic substitution of the "readily removed" thiophosphoryl group by the chloride anion takes place in stage (*a*). In stage (*b*) the ambident phosphorothioate anion attacks via its harder centre (the oxygen atom) the electrophilic phosphorus atom, which leads to the formation of dichloro-oxaphospholen and phosphorochloridothioate.

Together with the hypothesis of the formation of various open-chain and cyclic products in the reactions of phosphorylated allenes with sulphenyl chlorides, put forward as a possible explanation in a number of studies,[13,95,107] the following scheme has been discussed.[110] Four directions of attack on the allene system by the sulphenyl chloride molecule are possible in principle: at the 1,2- and 2,3-double bond in the *syn*- and *anti*-positions relative to the bulky substituent R^3 or P=O located correspondingly in the plane of the reacting double bond. Taking into account the electronic and steric factors, one can assume that there is a greater probability of attack by the sulphenyl chloride on the more nucleophilic 2,3-double bond of the phosphorylallene in the *anti*-position relative to the phosphoryl group [pathway (*a*) in the Scheme].

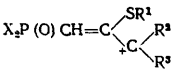
The nucleophilic cooperation of the phosphoryl oxygen in the attack by the sulphenyl chloride greatly facilitates the process and leads to the formation of the quasi-phosphonium intermediate (XXII). Subsequent attack by the chloride anion on the possible electrophilic centres of the quasi-phosphonium intermediate determines three main reaction pathways:

(1) If R^2, R^3 = H, then, regardless of the character of the substituents at the phosphorus atom, the attack by the chloride anion is directed to the carbon atom in the 5-position in the ring, which is the most electrophilic centre in the intermediate. This leads to intramolecular dealkylation with opening of the ring and the formation of the product of addition to the 2,3-double bond of the open-chain structure.

(2) When R^2, R^3 = Alk and X = AlkO, the attack by the chloride anion is directed to the carbon atom of the alkoxy-group and, in conformity with the second stage of the Arbuzov reaction, the quasi-phosphonium salt is dealkylated with elimination of the alkyl chloride and the formation of an oxaphospholen. When R^3 = H and X = OC_2H_5, the electrophilicities of the carbon atom of the alkoxy-group and of the C(5) atom of the intermediate are probably similar and for this reason the competing intramolecular and intermolecular dealkylation reactions take place and linear and cyclic products are formed.

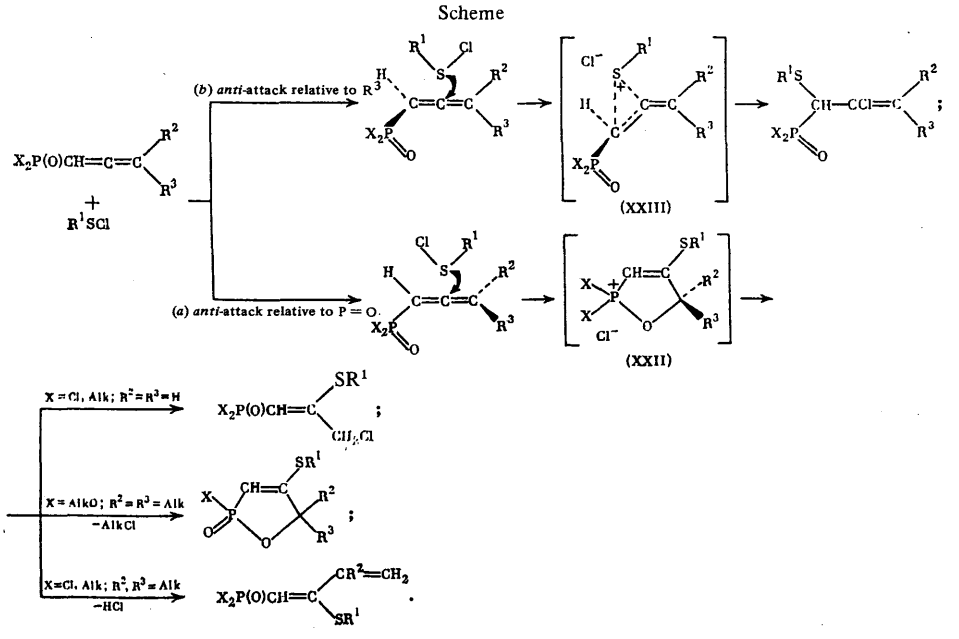
(3) When R^2, R^3 = Alk and X = Cl, Alk, whereupon the second stage of the Arbuzov reaction is impossible, the attack by the chloride anion is directed to the hydrogen atom of one of the alkyl substituents in the 5-position in the ring. HCl is eliminated and products with a diene structure are formed.

However, one cannot rule out the possibility that the formation of the 2,3-adduct and products with a diene structure is caused by the appearance of the carbenium ion



and takes place by-passing the quasi-phosphonium salt (XXII) stage.[107,118]

Scheme



The formation of 1,2-adducts can be accounted for solely by the attack by the sulphenyl chloride on the 1,2-double bond via pathway (*b*). According to generally accepted ideas,[122] the addition proceeds via the formation of a cyclic ion (XXIII) as an intermediate.[110,118] It may be that the addition takes place via a carbenium ion, which arises following the opening of the cyclic ion (XXIII).

4. Nucleophilic Addition to Phosphoryl Allenes

In the presence of alkali metal alkoxides, alcohols, dialkylphosphorous acids,[123,124] mercaptans,[125] and CH acids (acetoacetic and malonic esters and their homologues and cyanoacetic and phosphonoacetic esters)[125] readily add to the esters of 3,3-disubstituted allenylphosphonic acids at the 1,2-double bond activated by the electron-accepting phosphoryl group. Amines add in the absence of alkoxides also at the 1,2-double bond:[124]

$$(RO)_2P(O)CH{=}C{=}C(CH_3)_2 + XH \xrightarrow{RONa} (RO)_2P(O)CH_2{-}CX{=}C(CH_3)_2;$$

$$X = OR, NR_2, SR, CR(COOC_2H_5)_2,$$

$$CR(COOC_2H_5)_2(COCH_3),\ CR(COOC_2H_5)_2(CN),\ CR(COOC_2H_5)_2[P(O)(OC_2H_5)_2].$$

The attack by the nucleophilic anion is directed to the central *sp*-hybridised carbon atom of the cumulene. The structure of the adducts has been demonstrated by their ozonisation, by oxidation with potassium permanganate, and by hydrolysis.[124] The degree of the addition reaction and the structure of the products formed are determined by the degree of substitution at the sp^2-hybridised carbon atoms of the allenylphosphonates. Thus only one dialkyl phosphite molecule adds to the 1,2-double bond of the esters of 3-methylbuta-1,3-dienylphosphonic acid with formation of the corresponding bisphosphonates.[124] In the case of buta-1,2-dienylphosphonic acid, small amounts of trisphosphonates are formed together with the bisphosphonates, the yield of the former increasing when esters of buta-2,3-dien-2-ylphosphonic acid are used[126]

$$(RO)_2P(O)CR^1{=}C{=}CHR^2 + (R^3O)_2POH \xrightarrow{RO^-} (RO)_2P(O)CH(R^1){-}C(P(O)(OR^3)_2){=}CHR^2 \rightarrow$$

$$\rightarrow (RO)_2P(O)CH(R^1){-}CH(P(O)(OR^3)_2){-}CH{-}P(O)(OR^3)_2.$$

$R^1, R^2 = H, CH_3$

$R, R^3 = Alk$

These differences can be explained by the decrease of the steric hindrance in the sequence:[126]

$$(CH_3)_2C{=}C{=}CHP(O)(OR)_2 > CH_3(H)C{=}C{=}CHP(O)(OR)_2 > CH_2{=}C(CH_3)P(O)(OR)_2.$$

The esters of 3,3-unsubstituted allenylphosphonic acid combine with dialkyl phosphites to form, together with trisphosphonates, mixtures of the isomeric bisphosphonates: 1,2-bis(dialkylphosphono)prop-2-ene and 1,2-bis(dialkylphosphono)prop-1-ene.[126] Evidently, the partial prototropic allene–acetylene isomerisation of propadienylphosphonate to propynylphosphonate with the subsequent addition of the dialkyl phosphite to the triple bond leads to the formation of 1,2-bis(dialkylphosphono)prop-1-enes. ^{1}H NMR data have shown that the addition of dialkyl phosphites to 3-monosubstituted allenylphosphonates is not accompanied by the migration of the 2,3-double bond: it is retained in the adduct and the *cis*-disposition of the proton and the phosphoryl group is observed.

Isomerisation is likewise not observed in the addition of a mercaptan to diethyl buta-1,2-dienylphosphonates.[127] Propadienylphosphonates interact with mercaptans to form adducts with one and two addend molecules.[127] The formation of such adducts is possible also in the prototropic isomerisation of the products of addition to the 1,2-double bond of the cumulene, formed initially, to the thermodynamically more stable 1-dialkylphosphono-2-organylthioprop-1-ene [pathway (*b*)]:

$$(RO)_2P(O)CH{=}C{=}CH_2 \rightarrow$$

$$\xrightarrow[RONa]{R^1SH,} \begin{cases} \xrightarrow{(a)} (RO)_2P(O)C{\equiv}CCH_3 \xrightarrow{R^1SH} (RO)_2P(O)CH{=}C(SR^1)CH_3 \\ \xrightarrow{(b)} (RO)_2P(O)CH_2{-}C(SR^1){=}CH_2 \xrightarrow{R^1SH} (RO)_2P(O)CH_2C(SR^1)_3; \end{cases}$$

The interaction of dialkyl 1-methoxybuta-2,3-dien-2-ylphosphonates with ethanethiol in the presence of sodium mercaptide results in the formation of 3-ethylthio-1-methoxybut-3-en-2-ylphosphonates. The latter readily undergo prototropic transformations with migration of the double bond to the phosphonate group and the formation of 3-ethylthio-1-methoxybut-2-en-2-ylphosphonates:[128]

$$(RO_2)P(O)C{=}C{=}CH_2 + HSC_2H_5 \xrightarrow{C_2H_5SNa} (RO)_2P(O)CH(SC_2H_5)(CH_2OCH_3){-}C{=}CH_2 +$$

$$+ (RO)_2P(O)C(SC_2H_5)(CH_2OCH_3){=}C{-}CH_3.$$

The addition of alcohols to 1-alkoxybuta-2,3-dien-2-ylphosphonates leads to the formation of the isomeric *E*- and *Z*-esters of 1,3-dialkoxybut-2-enylphosphonic acid (*E* : *Z* = 2 : 1).[39,129] Evidently, the composition of the product is determined by the thermodynamic control of the reaction with the intermediate formation of the carbanion (XXIV):

$$(RO)_2P(O)C{=}C{=}CH_2 \rightarrow [(RO)_2P(O)\bar{C}{-}C{=}CH_2 \leftrightarrow (RO)_2P(O)C{=}C{-}\bar{C}H_2] \rightarrow$$

(XXIV)

$$\rightarrow (RO)_2P(O)C(CH_3){=}C(OR^2)R^1OCH_2 + (RO)_2P(O)C(OR^2){=}C(CH_3)R^1OCH_2.$$

E *Z*

It is noteworthy that the interaction of alcohols with 1-alkoxy-4-methylpenta-2,3-dienylphosphonates results in the formation of 3-alkoxy-2-phosphonoalka-1,3-dienes:[129]

$$(RO)_2P(O)C(CH_2OR^1){=}C{=}C(CH_3)_2 \rightarrow (RO)_2P(O)\bar{C}(CH_2OR^1){-}C(OR^2){=}C(CH_3)_2 \rightarrow (RO)_2P(O)CH(CH_2OR^1){-}C(OR^2){=}C(CH_3)_2.$$

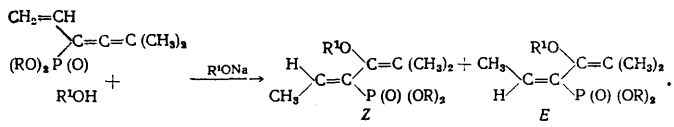
Unsubstituted phosphorylallenes combine with one alcohol molecule:[130]

$$(C_6H_5)_2P(O)CH{=}C{=}CH_2 + ROH \xrightarrow{RONa} (C_6H_5)_2P(O)CH{=}C(OR)(CH_3) \xrightarrow{H_2O}$$

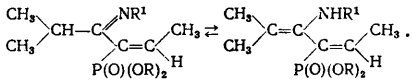
$$\rightarrow (C_6H_5)_2P(O)CH_2COCH_3.$$

3-Methyl-1-vinylbuta-1,2-dienylphosphonates readily interact with alcohols[131,132] to form 1,4-adducts, which are mixtures

of the *E*- and *Z*-isomers:

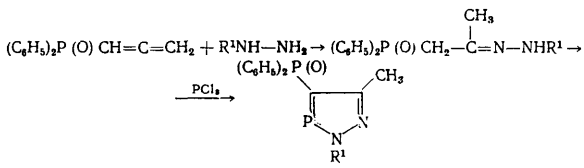


The interaction of secondary amines with 3-methyl-1-vinylbuta-1,2-dienylphosphonates also makes it possible to obtain diene phosphonates with the *trans*-disposition of the methyl and phosphoryl groups, whose formation is possible either as a result of addition to the 1,2-double bond of the allene and subsequent prototropic isomerisation or as a consequence of 1,4-addition. The use of primary amines in these reactions leads to the formation of a tautomeric mixture of imines and enamines:[133]

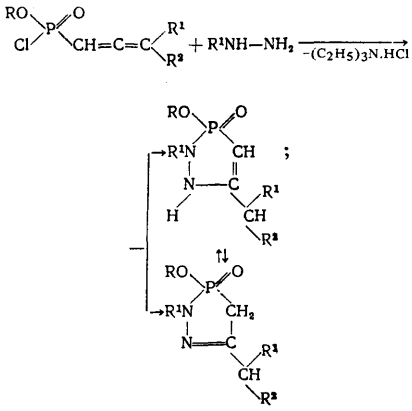


Dialkyl 1-methoxybuta-2,3-diene-2-ylphosphonates react with diethylamine to form 3-diethylaminobuta-1,3-dien-2-ylphosphonates.[134]

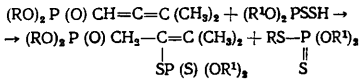
Interesting results have been obtained in the study of the interaction of phosphorylallenes with hydrazines:[130,135]



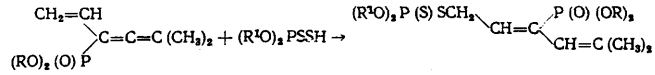
The use of the mono- and di-chlorides of allenylphosphonic acids in these reactions leads to intramolecular cyclisation:



OO-Dialkylphosphorodithioic acids interact with allenylphosphonates to form mixtures of products of addition to the 1,2-double bond of the cumulene and alkylation products—the full phosphorodithioate esters:[136]



In the reaction of 3-methyl-1-vinylbuta-1,2-dienylphosphonate the mode of addition of dialkylphosphorodithioic acids changes:[137]

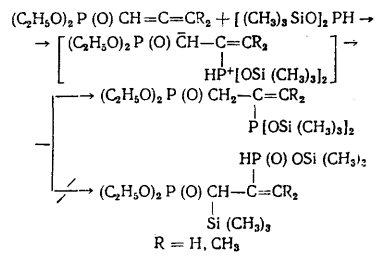


In a study of the interaction of vinylallenylphosphonates with acetylacetone, which is a CH acid, 1,2,4,5-disubstituted [tetrasubstituted? (Ed. of Translation)] benzenes were obtained unexpectedly in addition to the 1,4-adducts.

Alcohols, diethylamine,[139,140] and piperidine[141] add to the 1,2-double bond in quaternary 3-monosubstituted allenylphosphonium salts. The interaction of allylmercaptan with quaternary allenylphosphonium salts results in the formation of a mixture of products of addition to the 1,2- and 2,3-double bonds of the cumulene, which is associated with the partial prototropic isomerisation of the 1,2-adduct formed initially.[140]

5. Reactions With Derivatives of Tervalent Phosphorus

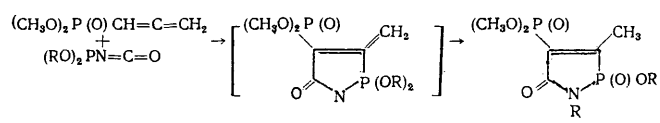
In the reaction of propa-dienyl- and 3-methylbuta-1,2-dienylphosphonates with bis(trimethylsilyl) hypophosphite the nucleophilic attack by the tricoordinate phosphorus is directed to the central carbon atom of the allene system. The intermediate dipolar ion is stabilised as a result of the migration of a proton:[142]



The prototropic isomerisation of propadienylphosphonate to propynylphosphonate is not observed under the reaction conditions.

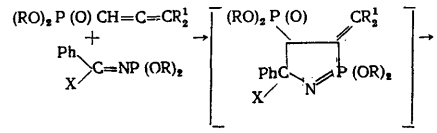
The reactions of allenylphosphonates with tervalent phosphorus derivatives containing an αβ-unsaturated fragment constitute a convenient method of synthesis of organophosphorus heterocycles.[2] The extensive experimental data which have accumulated hitherto on the reactions of these or "organophosphorus 1,3-dipoles" with alkenes and alkynes suggest that the interaction proceeds as a two-stage process and not as concerted [3 + 2]cycloaddition.

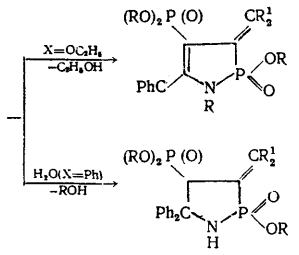
Dialkyl phosphoroisocyanatidite adds to the 1,2-double bond of allenylphosphonates:[143]



It is noteworthy that, under the cycloaddition conditions, the phosphoroisocyanatidite does not catalyse the isomerisation of allenylphosphonate to propynylphosphonate.

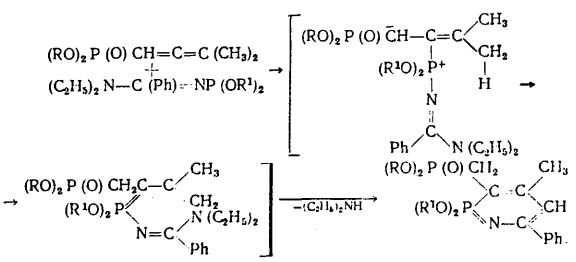
The reactions of *N*-diphenyl- and *N*-phenylethoxymethylenephosphoramidites with 3,3-disubstituted allenylphosphonates lead to the formation of the hydrolytically unstable five-membered azaphospholens with a P=N bond:[144]



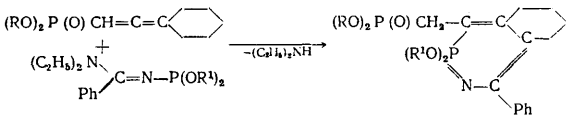


X=Ph, OC_2H_5;
$R^1=CH_3$, $R_2^1=(CH_2)_5$

However, *N*-phenyl(diethylamino)methylenephosphoramidites give rise to stable six-membered azaphosphorines under the same conditions in accordance with the following scheme:[145]

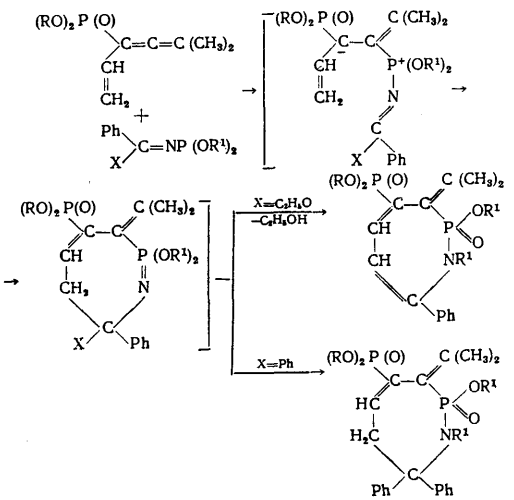


The reaction apparently begins with nucleophilic attack by the tervalent phosphorus atom on the central carbon atom of the allene system. The dipolar ion formed is stabilised by prototropic isomerisation and cyclisation with elimination of diethylamine. The interaction of cyclohexylidenevinylphosphonate with *N*-phenyl(diethylamino)methylenephosphoramidite results in the formation of a bicyclic adduct:

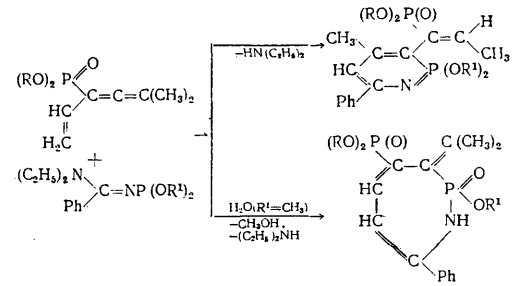


R=CH_3, C_2H_5, iso-C_3H_7; R^1=CH_3, C_2H_5

The introduction of a new reaction centre into the molecule of the 3,3-disubstituted allenylphosphonate (the vinyl group) results in the participation of the latter in the stabilisation of the intermediate dipolar ions formed in the reaction of 3-methyl-1-vinylbuta-1,2-dienylphosphonates with *N*-diphenyl- and *N*-phenyl(ethoxy)-methylenephosphoramidites:[146]



The structure of the seven-membered phosphepins was established by analysing their ^1H and ^{31}P NMR and mass-spectrometric data. 3-Methyl-1-vinylbuta-1,2-dienylphosphonates react with *N*-phenyl(diethylamino)methylenephosphoramidites to form six-membered azaphosphorines[146] similarly to 3-methylbuta-1,2-dienylphosphonates. However, this reaction pathway is not the only one: signals indicating the formation of azaphosphepines have been detected in the ^1H NMR spectrum of the reaction mixture. Crystalline azaphosphepine is the main product of the reaction of diethyl 3-methyl-1-vinylbuta-1,2-dienylphosphonate with dimethyl *N*-phenyl(diethylamino)methylenephosphoramidite:



Propadienylphosphonate does not react with *N*-methylenephosphoramidites, isomerising to propynylphosphonate in their presence.[145]

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It follows from the data examined that phosphorylated allenes can be used successfully in the synthesis of a wide variety of organophosphorus compounds. By varying the degree of substitution and the character of the substituents at the sp^2-hybridised carbon atoms of phosphoryl allenes, it is possible to activate a particular unsaturated reaction centre in the molecule. As a result of the introduction of the electron-accepting phosphoryl group into the allene molecule, the initial step of the reaction with nucleophiles is attack by the anion on the central carbon atom of the cumulene with the subsequent addition of a proton to the C(1) carbon atom. The stability of the product formed depends to a large extent on the character of the substituents at the C(3) carbon atom of the allene and on the basicity of the reacting anion, which promotes to some extent the prototropic isomerisation. The addition of electrophiles proceeds mainly at the 2,3-double bond of phosphorylallenes, also with the initial attack on the central *sp*-hybridised carbon atom, and, depending on the character of the substituents at the C(1) and C(3) atoms, leads to the formation of either products having open-chain alkene or diene structures or to heterocycles with participation of the phosphoryl group.

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