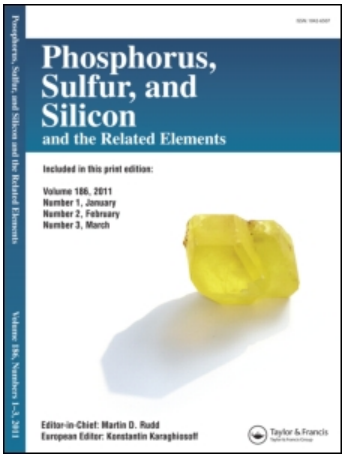

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FIVE-MEMBERED HETEROCYCLIZATION OF PHOSPHORUS-CONTAINING ALLENES BY THEIR REACTION WITH ELECTROPHILES—POSSIBILITIES AND RESTRICTIONS

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FIVE-MEMBERED HETEROCYCLIZATION OF PHOSPHORUS-CONTAINING ALLENES BY THEIR REACTION WITH ELECTROPHILES—POSSIBILITIES AND RESTRICTIONS

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In the past several years the reaction ability of phosphorylated allenes with electrophilic reagents has been intensively studied. The experimental data showed that during the interaction of reactants a cyclization of allenic system of π-bonds and phosphorylic group (O=P—C=C=C) takes place leading to the formation of P,O-containing heterocyclic compounds.

The present paper generalizes the results obtained so far, allowing a critical assessment of the conditions and restrictions for the realization of this interesting reaction.

I. INTRODUCTION

Unsaturated P-organic compounds, whose methods of synthesis have been worked out recently increasingly attract attention of organo-phosphorus chemists, because of their high reactive ability and interesting chemical transformations. A particular place among these compounds is taken by the phosphorylated allenes which are easily obtained, via acetylene-allene rearrangement of acetylene phosphites—prepared from α-alkynols and trivalent phosphorus compounds:[1-10] This rearrangement turned out to be a convenient and unique method of synthesis of 1,2-alkadienylphosphonates and phosphinates and also tertiary allenic phosphine oxides. The availability of this method, the large variety of compounds which are obtained by this reaction, and the interesting system of double bonds which they contain, very soon allowed systematic investigations of their chemical behaviour towards a series of other reagents. The studies in this field increased markedly after the heterocyclization of phosphorus-containing allenes in reaction with halogens to give five-membered ring system was discovered. This added a new type of chemical transformation to organo-phosphorus chemistry, connected with the synthesis of rare derivatives of 1,2-oxaphosphol-3-ene. For a short period of time a series of papers were published dealing with the heterocyclization, observed not only during the halogenation but also during the interaction with sulfenyl chlorides, hydrogen chloride and other electrophilic reagents.

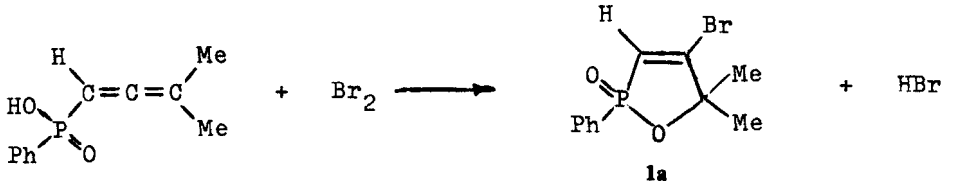
The publications which have appeared, thus far, allow some generalizations to be made and to discuss the possibilities and restrictions for the synthesis of P,O-containing five-membered heterocycles from phosphorylated allenes and electrophilic reagents.

For the purpose of the systematic discussion of the experimental data in the present review the classification of electrophilic reagents according to C. K. Ingold was used,[11] involving a division into two main groups: 1. electrophiles having non-acid character, such as halogens, sulfenyl, selenyl chlorides etc. and 2. acid electrophiles like hydrogen chloride and other strong acids.

II. ALLENIC ORGANO-PHOSPHORUS COMPOUNDS IN REACTIONS WITH NON-ACIDIC ELECTROPHILIC REAGENTS

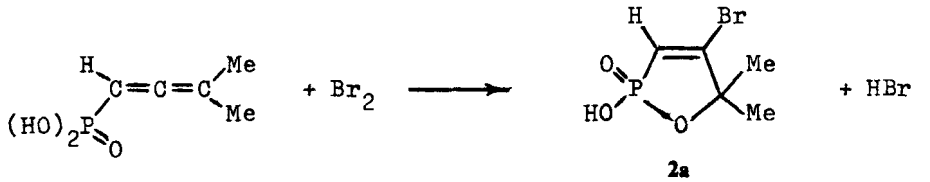
1. Halogenation of 1,2-alkadienephosphinic and phosphonic acids and their derivatives

It should be noted at the beginning that the interaction of allenic phosphinic and phosphonic acids with halogens and other non-acidic electrophiles has not been well studied, and only two papers have been published concerned with the bromination of these compounds. S. Braverman and D. Reisman,[12] studying the behavior of a group of substituted allenes, containing an electron acceptor group, found that phenyl-3-methyl-1,2-butadienylphosphinic acid undergoes cyclization, reacting with bromine to form 4-bromo-2-phenyl-2-oxo-1,2-oxaphosphol-3-ene **(1a)**:



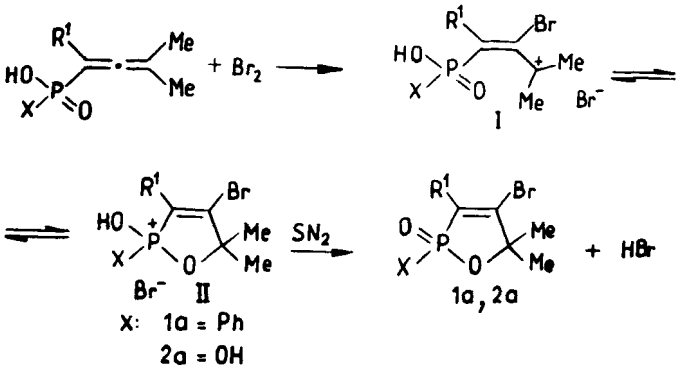
1a

3-Methyl-1,2-butadienylphosphonic acid, with the same reagent, forms the 2-oxy-1,2-oxaphosphol-3-ene **2a**:



2a

The authors suggest the intermediate formation of a tertiary carbonium ion I which is in equilibrium with the quasiphosphonium salt II (see Scheme 1). From the latter, elimination of hydrogen bromide produces the oxaphospholene, with tetra-coordinate phosphorus **1a, 2a**.

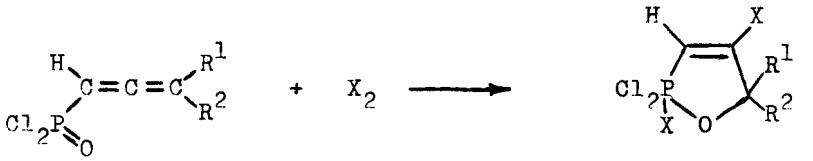


Scheme 1

In a number of publications R. S. Macomber examined the reactivity of allenic phosphonic acids with electrophiles. He showed that in the bromination of these compounds cyclization is also possible at the monosubstituted C^3 atom of the allenic bond.[13] It is suggested in the intermediate stage a bromonium or secondary carbonium ion are involved.

The above authors did not describe the stabilization of the carbonium ions by an allylic rearrangement, which is less likely because of the destabilization of the double bond adjacent to the phosphoryl group.

It has been established that in the halogenation of allenylphosphonic dichlorides the course of the reaction depends on the substituents at the C^3 atom of the allenic bond. The disubstituted 1,2-alkadienylphosphonates give rise to a cycloaddition of the reagent with formation of tetrahalo-1,2-oxaphosphol-3-enes **3**:[14,15]

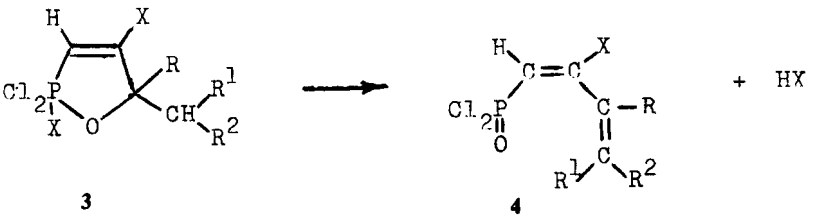


3

If $R^1 + R^2 = (—CH_2—)_5$ spiro compounds are formed.[16] In the case of 3-monosubstituted dichlorides and the allenylphosphonic dichloride cyclization is not observed. The halogenation proceeds with formation of complicated mixtures of products, resulting from the addition to the double bonds.[17]

The synthesis of 2,2-dichloro-2,4-dihalogeno-1,2-oxaphosphol-3-enes **3** is accompanied by a comparatively rare change of the bond symmetry of the P-atom from tetrahedral to trigonal-bipyramidal ($P^{IV} \rightarrow P^{V}$). It is most characteristic for the halogenation of the thiophosphoryl derivatives.[18]

The phosphoranes **3** are stable in nonpolar solvents for a period of several days. Upon storage they evolve hydrogen halide and just the opposite change in the valence state of the P-atom takes place ($P^{V} \rightarrow P^{IV}$), which is due to the formation of 2-halo-1,3-alkadienylphosphonic dichlorides **4**:[15,19]



3 **4**

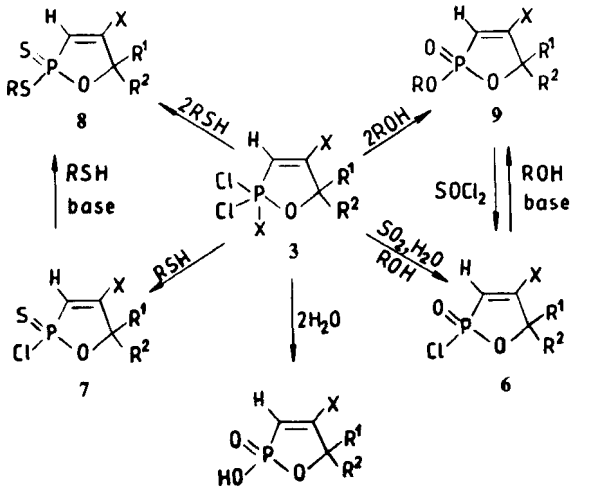
In polar solvents, such as chloroform, nitromethane etc., the evolution of hydrogen halogenide becomes faster. The elimination is accelerated by heating or by removing the solvent. Frequently, it commences not before the solvent has been entirely removed. The evolution of hydrogen halide then is very energetic process, accompanied by heating of the reaction mixture, i.e. this reaction proceeds towards formation of a thermodynamically stable product. During the evolution of hydrogen halide there is no secondary interaction of the latter with the 1,3-dienic system formed concurrently. It should be noted that hydrogen bromide is eliminated more readily than hydrogen chloride and in several cases during the bromination in polar solvents it is not possible to obtain the phosphorane **3**. Probably, the bromine derivatives of pentavalent phosphorus have a strongly polar structure.[19]

The formation of the 1,3-dienylphosphonates **4** from **3** suggests that the double bonds in these compounds are in s-cis-conformation, which was proved by ^{1}H-nmr spectral studies with the help of lanthanide shift reagents.[20] Recently the structure of **4** was confirmed also by the reaction with electrophiles. For example, in the halogenation of 1,3-dienylphosphonates, obtained according to the method described

above, heterocyclization with formation of a six-membered ring system (5,6-dihydro-2H-1,2-oxaphosphorine derivatives) takes place.[21-23] Compounds of type **4**, synthesized according to other methods (s-transconformation),[24,25] do not lead to formation of P-containing heterocycles, but to products of addition of the halogen to the remote double bond.[26]

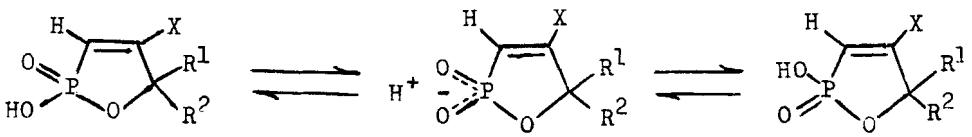
By hydrogen chloride elimination from **3**, containing a vinyl group at the C^3 atom of the ring alkatrienylphosphonic dichlorides have recently been synthesized.[27]

The phosphoranes **3** are compounds of high reactivity. They exhibit chemical transformations typical of halides of pentavalent phosphorus. A great variety of 1,2-oxaphosphol-3-ene derivatives obtained by interaction with water, alcohols ect., is presented in Scheme 2:[28,29]



Scheme 2

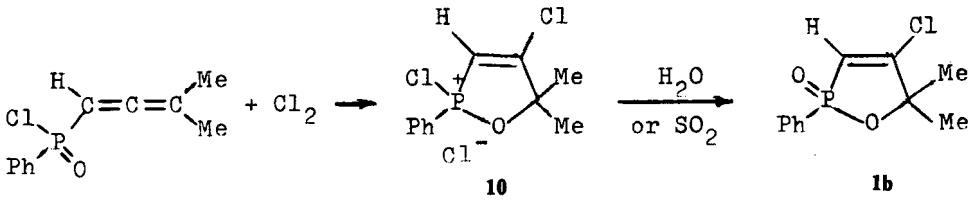
The difference between **3** and **6–9** is that the latter have a chiral phosphorus atom, which renders substituents R^1 and R^2 non-equivalent if they are identical: diastereoisomeric mixture are formed if these substituents are different. The P-atom is losing its chirality in the cyclic acids, but when the substituents at the C^5 atom in the ring are different, diastereoisomers are not formed, which is explained by the ionic structure and the fast exchange of the proton between the two oxygen atoms:



2, 5 X: 2 = Br, 5 = Cl

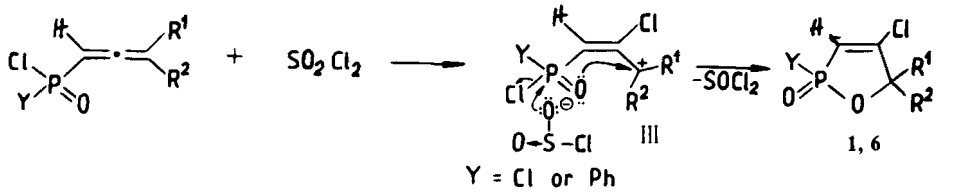
The structural features of the 1,2-oxaphosphol-3-enes suggest that either the five-membered ring is situated in a plane or a fast transformation of the different spatial conformers into one another, is occurring which is in good agreement with the X-ray structural studies of similar systems.[30]

The experimental data show that the chlorination of phenyl-3-methyl-1,2-butadienylphosphinic chloride leads to the phosphonium chloride **10**. The latter is extremely hygroscopic and through exposure to moist air or upon treatment with sulfur dioxide turns into an oxaphospholene with tetracoordinated phosphorus:[30]



10 1b

The cyclization of chlorides of allenylphosphinic and phosphonic acids to form five-membered heterocycles can be induced by their interaction with sulfuryl chloride. In this case not only di-substituted but also mono-substituted at C^3 atom phosphorylated allenes gives 1,2-oxaphosphol-3-ene derivatives:[31,32]



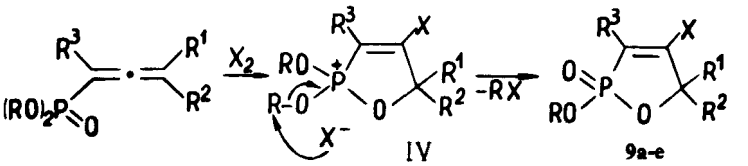
III 1, 6

Y = Cl or Ph

Scheme 3

It is most likely that cyclic tetrahalides **3**, described earlier are not formed as intermediates. Rather, it is assumed that they form via the carbonium ion III, by a synchronous nucleophilic attack of the phosphoryl oxygen atom on C^3 and the same attack of one of the O-atom in the sulfo-group at phosphorus. As a result of all this the allenephosphonate π-electron system is closed with formation of a ring with the elimination of chloride ion from the P-atom. The latter adds to the S-atom of the reagent and is released as thionyl chloride. In the interaction with SO_2Cl_2 the only exception is allenylphosphonic dichloride which leads to the formation of a complicated mixture of products of addition to the double bonds, as in the course of the chlorination.

The halogenation of 1,2-alkadienylphosphonic dialkyl esters also proceeds through heterocyclization:[33,34]



IV 9a-e

Scheme 4

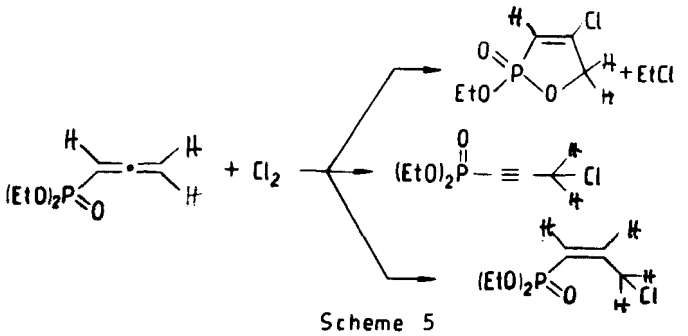
9	X	R^1	R^2	R^3
a	Cl,Br I	Me	Me,Et ect.	H
b	Cl,Br	H	Me	H
c	Cl	H	H	Me
d	Cl	H	H	H
e	Cl,Br J	cyclohexyl		H

Here, unlike the case of the phosphoranes **3** alkyl halide is eliminated and 1,2-oxaphosphol-3-ene-2-oxides are formed. The rate of the reaction depends on the nature of the halogen; chlorine and bromine require cooling while the bromine reaction is a weakly exothermic process. Iodine, at ambient temperature, is not reacting significantly with the allene bond and the process starts by heating of the reaction mixture.[35]

The experimental data discussed above differ from the results of A. N. Pudovik *et al.*[36] who claim that in the bromination of 3,3-disubstituted allenylphosphonic esters an addition of the reagent to the C^2—C^3 double bond is taking place, followed by anionotropic isomerization of the dibromo-derivatives.

The formation of **9a–e** probably proceeds through a quasiphosphonium species IV, by analogy with the intermediate complex in the Arbuzov reaction. In the present case, however, IV is not sufficiently stable to be isolated, because of the fast second stage of the reaction—elimination of alkyl halide.

The five-membered heterocyclization of 1,2-alkadienylphosphonic esters with tertiary and secondary C^3 atoms or with tertiary C^1 and primary C^3 atoms is an indication for the high stereoselectivity of this reaction. Even in the case of the chlorination of 1,2-propadienylphosphonic esters, small amounts of 1,2-oxaphospholenic ester are observed by ^{1}H-nmr spectroscopy in the reaction mixture, although the main products of the reaction are 2,3-adducts and the propynylphosphonic derivatives:[17]

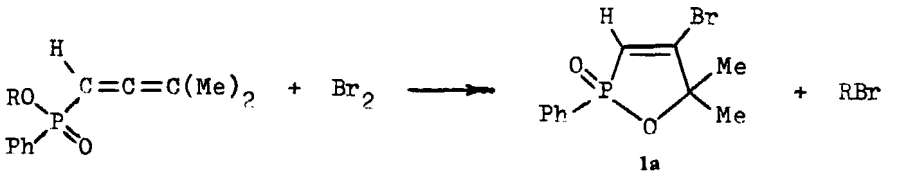


Scheme 5

The different course of the reaction of the substituted phosphonic esters and the esters of the propadienylphosphonic acid proves the substantial influence of the alkyl groups in the allenic bond system on the stabilization of the transition state, leading to a successful heterocyclization.

Sulfuryl chloride reacts with the 1,2-alkadienylphosphonic esters, where 1,2-oxaphosphol-3-ene-chloro derivatives are formed, but the 1,2-propadienylphosphonic esters are giving complicated reaction mixture in which the 2,3-adduct is predominating.[32]

Halogenation of the phenyl-1,2-alkadienylphosphinic esters leads to formation of oxaphospholene derivatives, as in the halogenation of the free acids:[12]

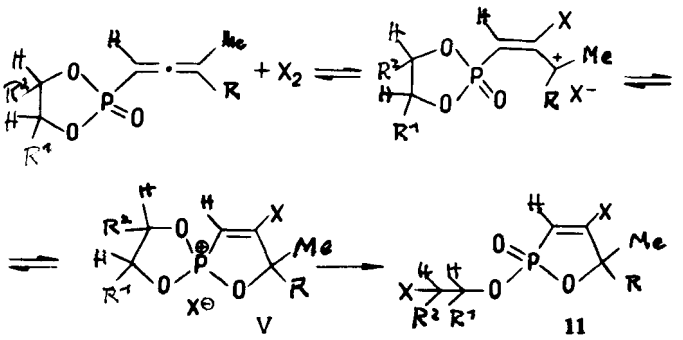


1a

In the same paper the bromination of the substituted allenylphosphonic esters, which leads to the synthesis of some of the esters, **9** is described.

As shown in Scheme 2, the alkoxyderivatives, **9a–e**, by treatment with thionyl chloride are converted to cyclic chlorides, the latter reacting with aliphatic alcohols in the presence of organic base to give **9a–e**. It should be noted that the interaction with $SOCl_2$ is not always successful. For instance, the fact that compounds **9c** and **9d** are not forming chloride is connected to a large extent to the presence of substituents at the C^5 atom in the ring, which increase the electron density at the phosphorus atom, and facilitate the exchange reaction.

The allene-containing 2-oxo-1,3,2-dioxaphospholanes in an inert solvent, as distinct from the esters **9**, during the halogenation, are not eliminating alkyl chloride; instead cycloaddition of the reactants is observed. This is connected to the opening of the dioxaphospholane ring and formation of a new five-membered ring **11**:[37]

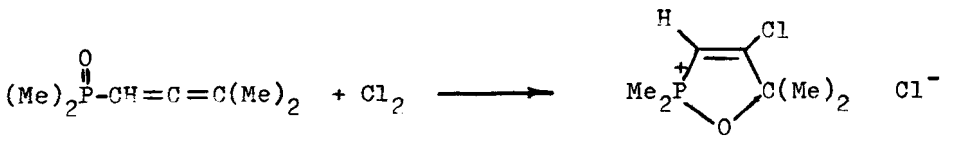


Scheme 6

The reaction proceeds exclusively towards oxaphospholene cyclization, which is confirmed by the ^{1}H-nmr spectra of the reaction mixtures, obtained immediately after the addition of the halogen to the initial allenylphosphonates. Probably, the reaction proceeds through a carbonium ion which in the next stage cyclisizes to spiro phosphonium salt V. The formation of V has not, as yet been proved because of the fast intramolecular rearrangement of the Arbuzov type leading to opening of the ring and addition of halide ion to the aliphatic part of the alcoxy group formed.

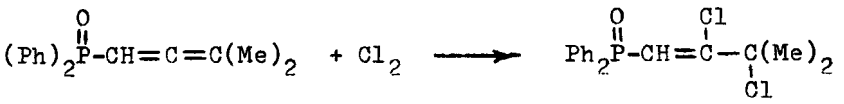
2. Chlorination of tertiary allene phosphine oxides

The tertiary allene phosphine oxides are less common then the derivatives of 1,2-alkadienylphosphinic and phosphonic acids. The study of their reactivity towards electrophiles, however, is quite interesting, because in this case if a heterocyclization of the allenylphosphonic system of π-bonds is carried out, it would lead to the formation of stable phosphonium salts. The second stage of an Arbuzov type reaction could be impossible here. The experimental investigations show, that the reaction route depends not only on the substituents at the allenic bond, but also on the nature of the other two hydrocarbon groups at phosphorus. For example, by reaction of the dimethyl-3-methyl-1,2-butadienyl-phosphineoxide with chlorine in CCl_4 a cyclic phosphonium salt, **12** is obtained:[31]



12

while the phenyl analogue of this oxide, under the same conditions, is adding chlorine to the C^2—C^3 double bond:



13

Compounds **12** and **13** are substantially different from one another by their spectral and other physical properties.[31]

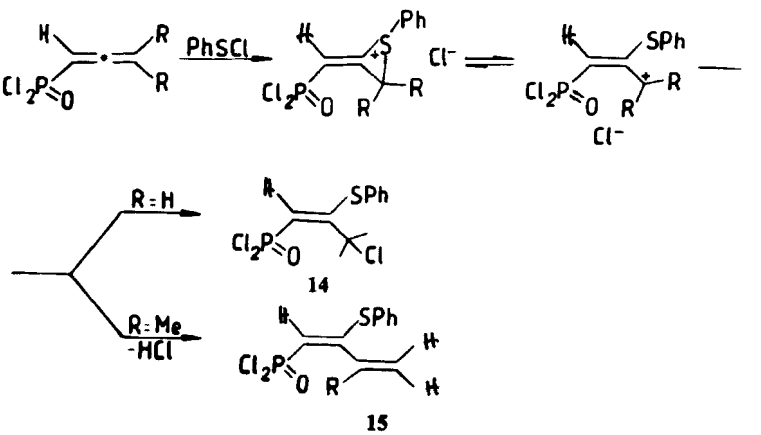
In the chlorination of diphenyl-1,2-butadienyl- and diphenyl-propadienyl-phosphineoxides 2,3-adducts are obtained, too.

The differences observed in the chlorination of tertiary allenic phosphineoxides may be due to the possibility of conjugation between phenylgroups and the phosphoryloxygen, which would decrease the nucleophilic properties of the latter for attack on the intermediate carbonium ion. Here, however, a greater role is played by the spatial effect of the P=O group on the geometry of the transition state, where the bulkier phenyl groups retard the cyclization and accelerate the addition. The last supposition is more likely, because it is known that the phosphorus atom is a bad transmitter of the conjugation.[38]

3. Interaction of 1,2-alkadienylphosphonates with sulfenyl chlorides

The reactions of sulfenyl chlorides with 1,2-alkadienylphosphonates are very intensively studied now. Recently in the literature data were published concerning the investigation of reaction the above mentioned reagents with 1,2-alkadienylphosphonic dichlorides and dialkylesters. Nevertheless, they enable a comparison to be made of the reactivity of sulfenyl chlorides and halogens with phosphorylated allenes.

The interaction of 1,2-alkadienylphosphonic dichlorides with phenylsulfenyl chloride depends on the substituents at the C^3 atom—either the reagent is added to the C^2—C^3 double bond (C^3 is a primary carbon atom), or 1,3-alkadienylphosphonic dichloride is formed (C^3 is a tertiary carbon atom):



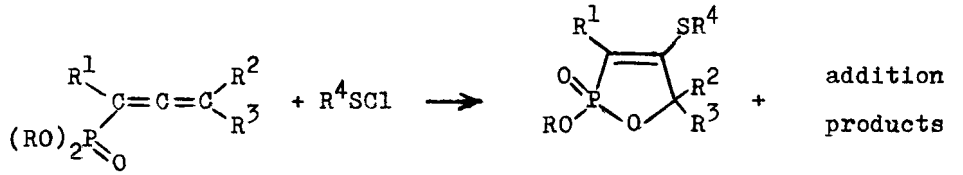
14

15

Scheme 7

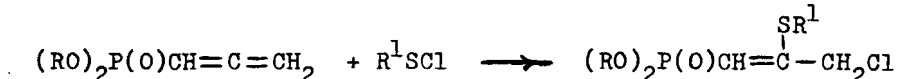
The authors[39] assume that the reaction proceeds through formation of an episulfonium ion, followed by the decomposition of the latter to a free carbonium ion.

Rather detailed studies of the reaction of 1,2-alkadienylphosphonic dialkyl esters with sulfenyl chlorides have already been accomplished. It is established that the compounds mentioned react according to the following general scheme:



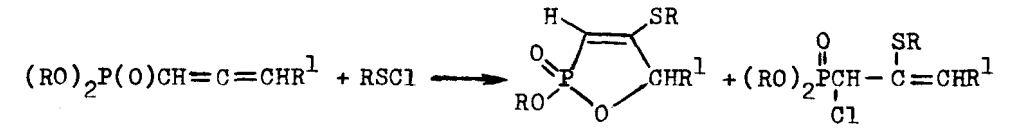
The reaction route strongly depends on the degree of substitution at the C^1 and C^3 atoms of the allenic system, on the nature of these substituents, and on the type of the hydrocarbon part of the sulfenyl chloride, all other conditions being equal.

A. N. Pudovik *et al.*[39] when studying the interaction of propadienyl phosphonic dimethyl ester with phenylsulfenyl chloride found that the latter is added to the C^2—C^3 double bond. Independently, working with other esters we reached the same conclusion:[40]



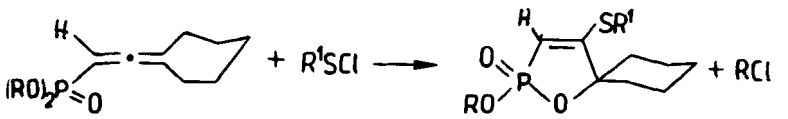
16

The interaction of alkylsulfenyl chlorides with C^3 monosobstituted 1,2-alkadienylphosphonic esters, in all cases, unlike the reagents with halogens, leads to the formation of a mixture of five-membered heterocycles and 1,2-adducts:[40]



17 **18**

3,3-Disubstituted 1,2-alkadienylphosphonic esters with sulfenyl chlorides give rise, mainly, to 1,2-oxaphosphol-3-ene-2-oxides.[41] When cyclohexylidene vinylphosphonic esters are used in the reaction, spiro compounds are obtained:[42]

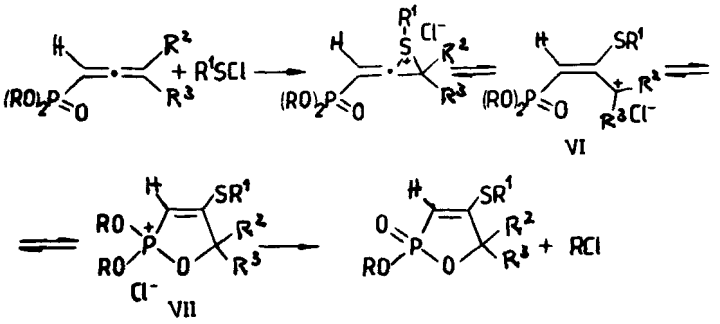


19

Scheme 8

If the C^5 atom in the ring is chiral, the isomers formed in the diastereomeric mixtures depend on the reaction temperature. When the temperature decreases an increase in the stereoselectivity of the reaction is observed, but over a larger tempera-

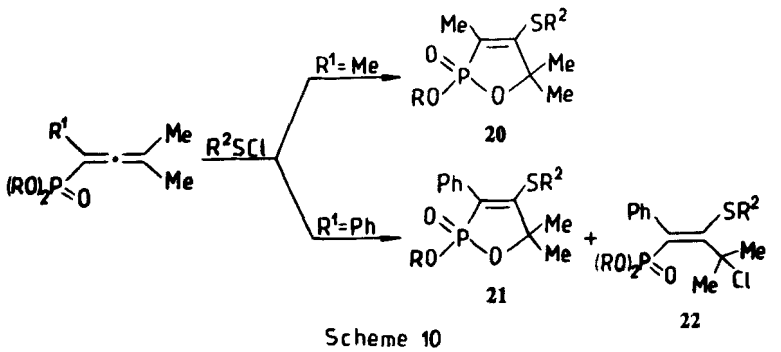
ture interval the selectivity is small.[43] This shows that for C^3 disubstituted esters the formation of quasiphosphonium compounds VII proceeds through a free carbonium ion VI:



Scheme 9

Detailed chromatographic studies of the reaction mixtures show that after the interaction of disubstituted esters with sulfenyl chlorides small amounts of 1,2-adducts are obtained.[43]

The trisubstituted allenylphosphonic esters, depending on the type of substituent at C^1 with sulfenyl chlorides either yield oxaphospholene esters **20, 21** or, together with the latter, form the 2,3-adduct **22**:[40]

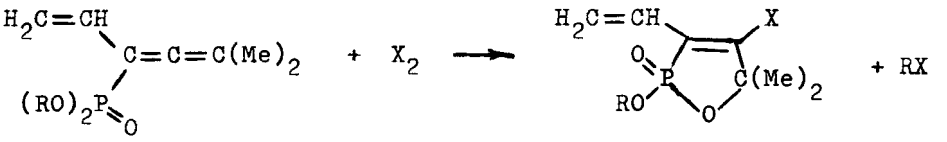


Scheme 10

When R^1 = Ph the formation of 2,3-adduct **22** in larger amounts is not unexpected. This substituent deactivates the C^1—C^2 double bond for electrophilic attack, from one side, which explains the absence of 1,2-adduct. Alternatively, the phenyl group sterically hinders the nucleophilic attack of the phosphoryl oxygen on the carbonium ion. The latter facilitates the addition of the chloride anion.

4. Alkatrienylphosphonic esters in reactions with halogens and sulfenyl chlorides

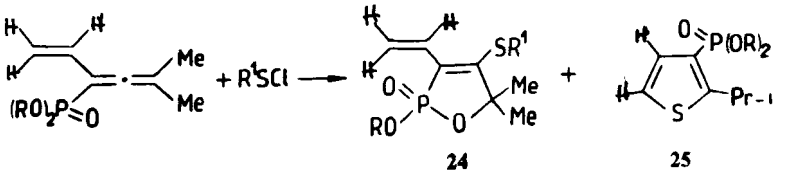
The C^1 or C^3 vinylsubstituted allenylphosphonic esters[9] contain a triene system of double bonds which have 1,2- and 1,3-diene sections. It may be suggested that such a combination of π-bonds would have a significant effect on the reaction route during their interaction with electrophiles. It was established by us that 5-methyl-1,3,4-hexatrienyl-2-phosphonic esters react with halogens with its 1,2-diene section; thus, 3-vinylsubstituted 1,2-oxaphosphol-3-enes **23** are obtained:[44]



23

^{1}H-nmr spectral studies of the reaction mixtures obtained immediately after the halogen has been added in the system show that the exclusive reaction route is towards oxaphospholene cyclization, i.e. the tertiary carbonium ion formed in the intermediate stage is practically not taking part in the allylic rearrangement with the neighboring double bonds.

When the electrophilic reagent is changed, a substantial change in the reaction route occurs. For example, with the same esters the alkylsulfenyl chlorides are giving a mixture of compounds **24, 25**, which are a result of oxaphospholene and thiophene cyclizations:[45]

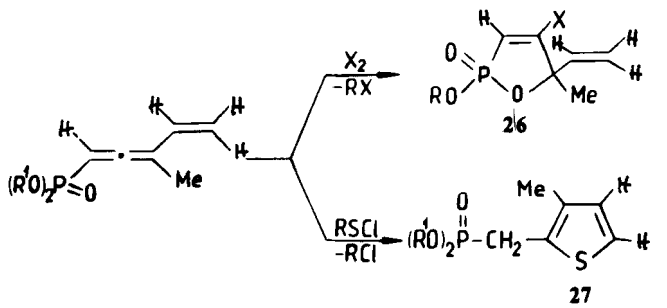


24 25

Scheme 11

At lower temperatures the 3-thienylphosphonic esters **25** predominates in the reaction mixture, but at higher temperatures the oxaphospholenic ester **24** is preferentially formed. Therefore, the lower temperatures are favoring the formation of cyclic sulfonium ion whereas higher temperatures are shifting the equilibrium towards formation of carbonium ion, which facilitate the oxaphospholene cyclization. The use of nonpolar solvent enabled the separation and identification of both compounds.

The significant difference between the halogens and the sulfenyl chlorides can best be seen when studying their interaction with 3-methyl-1,2,4-pentatrienyl-1-phosphonic esters. The latter with halogens are giving 5-vinyl-1,2-oxaphosphol-3-ene-2-oxides **26**[46] while with alkylsulfenyl chlorides—2-thenylphosphonic esters **27** are formed:[47]



26 27

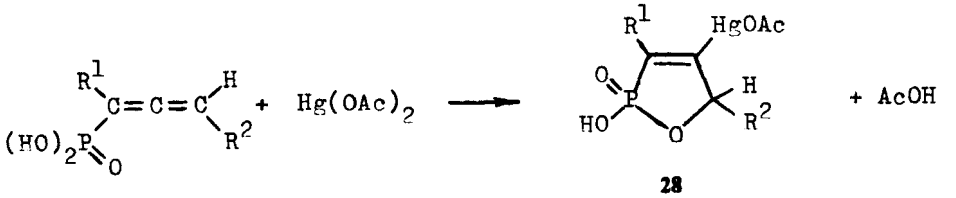
Scheme 12

The differences observed in the behavior of the halogens and the sulfenyl chlorides are related to the mechanism of their interaction with the alkatrienylphosphonates. Our investigations show that the halogenation proceeds through tertiary carbonium ions, which are promoting the formation of oxaphospholene cycles. The sulfenyl chlorides, however, have a tendency of forming episulphonium ions. In those cases where these ions can be stabilized by neighboring double bonds the reaction changes its direction and a new type of cyclization is observed. The thiophene cyclization is favored also by the possibility for prototropic isomerization of the five-membered sulfonium ion intermediate, which is facilitated by the aromatization of the five-membered heterocyclic system,[27] and formation of a thermodynamically stable product.[45,47] If this type of isomerization is not possible, the thiophene cyclization does not occur. An indirect confirmation of these contentions can be given by the 2-chloro-1,3-alkadienylphosphonic esters which with sulfenyl chlorides are leading to formation of five- or six-membered heterocycles in which the P=O group is taking part.[48]

5. Interaction of 1,2-alkadienylphosphonates with other nonacid electrophiles

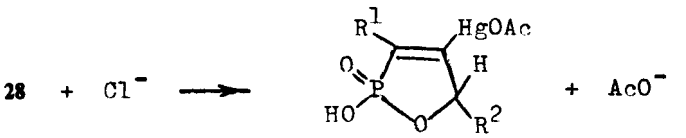
In the literature have been published only two papers dealing with the reaction ability of phosphorylated allenes with another non-acid electrophiles.

R. S. Macomber has observed that mercuric acetate in acetic acid causes five-membered heterocyclization of substituted allenephosphonic acids:[13]



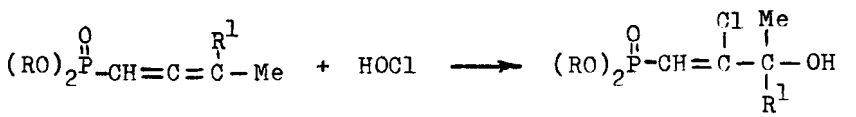
28

Compound **28** cannot be isolated and purified, but when treated with chloride anion it is converted to the chloride which may be isolated and identified:



29

In contrast to the halogens and sulfenyl chlorides hypochlorous acid with 3,3-disubstituted allenylphosphonic esters does not lead to the oxaphospholenic cyclization described above; instead 2,3-adducts **30** are obtained as reaction products:[49]



30

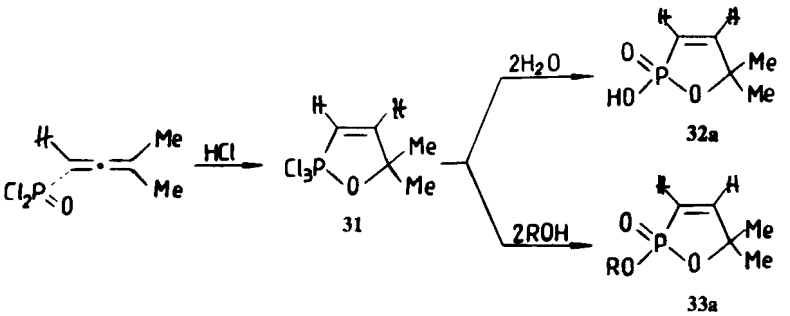
Presumably the nucleophilic activity of the hydroxyl group is insufficient to cause elimination of the aliphatic alcohol, which facilitates the addition of the reagent after the cyclization.

Our experiments concerning the reactivity of XCN, NO_2Cl, NOCl, Cl_3CSCl etc., we have found that all these do not interact with 1,2-alkadienylphosphonic esters within the chosen conditions (non-polar or weakly polar solvent and a large temperature interval).

III. PHOSPHORYLATED ALLENES IN REACTIONS WITH ACID ELECTROPHILIC REAGENTS

1. Hydrochlorination of 1,2-alkadienylphosphinates, phosphonates and tertiary allene phosphine oxides

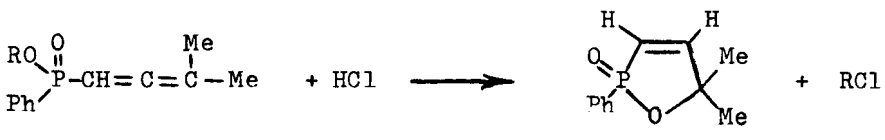
Studying the hydrochlorination of dichlorides of 3-mono- and 3,3-disubstituted allenylphosphonic acids in an inert solvent over a period of 24 hours, A. A. Petrov *et al.* have observed that no reaction is taking place. The initial compounds[50] are isolated from the reaction mixture. R. S. Macomber *et al.*, in contrast to the results described above showed that HCl can react with dichlorides of substituted allenylphosphonic acids to give cyclic phosphoranes **31**. The reaction is carried out in dichloromethane at ambient temperature over a period of 25 days:[51]



Scheme 13

When **31** is treated with water 1,2-oxaphospholenic acids **32a** are obtained whereas with aliphatic alcohols the esters **33a** of these acids are formed.

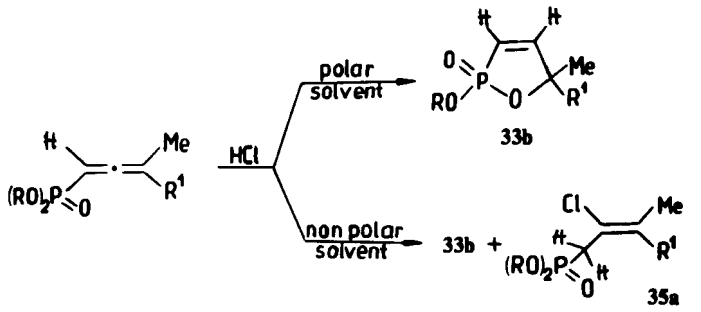
In the hydrochlorination of phenyl(3-methyl-1,2-butadienyl)phosphinic ester, a protophilic heterocyclization of the allenylphosphinate group takes place **34**:[52]



34

The formation of compounds with quasiphosphonium structure is not observed here.

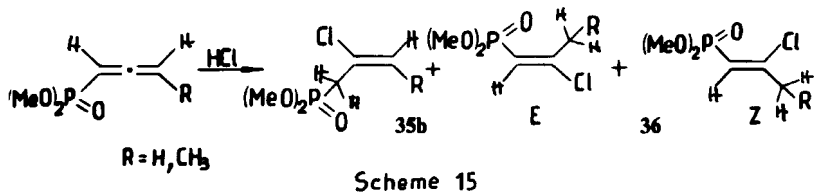
3,3-Disubstituted allenylphosphonic esters react with HCl, dependent on of the substituents to give oxaphospholenic esters **33b** or 1,2-adducts **35a**.[52,53] In polar solvents a protophilic cyclization is exclusively obtained:



Scheme 14

The presence of a phenyl group at the C^1 atom of the allene causes partial hydrolysis of the ester **33** to a cyclic acid. In non-polar solvents the reaction proceeds more slowly and its rate depends on the size of the hydrocarbon chain of the aliphatic substituents at the allenic bond or in the alloxy group. In these solvents the esters **33**, together with 1,2-adducts are formed. Only the 1,2-alkadienylphosphonic dimethyl esters make an exception, in that with HCl they are forming 1,2-oxaphosphol-3-ene derivatives, independent of the solvent polarity.

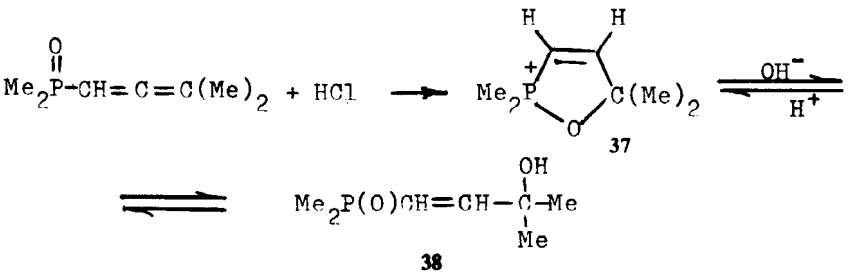
1,2-Alkadienylphosphonic esters with a secondary or primary C^3 atom, even in polar solvents, are not converted to cyclic compounds under the influence of HCl. The reaction is very difficult to initiate and a mixture of addition products is formed:



Scheme 15

The esters **33**, when treated with thionyl chloride are forming the respective chlorides. Upon interaction with PCl_5 opening of the ring occurs with formation of 1,3-dienylphosphonates.[52]

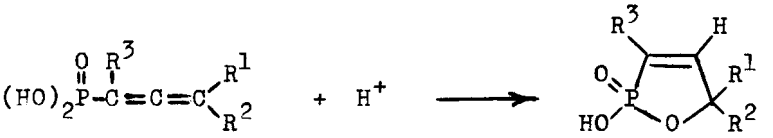
Dimethyl(3-methyl-1,2-butadienyl) phosphineoxide with HCl forms a cyclic phosphonium salt **37**:[54]



This salt is unstable in water and there is partial opening of the ring with formation of the oxide **38**. When the acidity of the solution is lower, the equilibrium moves towards the compound with straight chain and at pH 3 the ring is opened completely. This process of ring opening can be considered as a second stage of the Arbuzov rearrangement, taking into account that the process is reversible here, because if the acidity of the solvent is changed to pH 1, **37** is formed again.

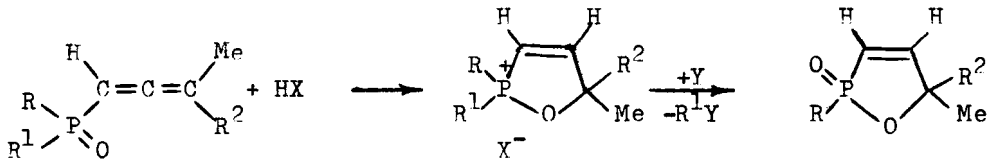
2. Protophilic heterocyclization of phosphorylated allenes under the influence of strong acids

R. S. Macomber[51] has observed that substituted allene phosphonic acids in aqueous solution are readily cyclized under the influence of mineral acids:



32b

The protophilic cyclization in an acidic medium can be carried out with other allene organophosphorus compounds.[52,54] This reaction proceeds with intermediate formation of a quasiphosphonium adduct **39**:[54,55]



39 **40a-e**

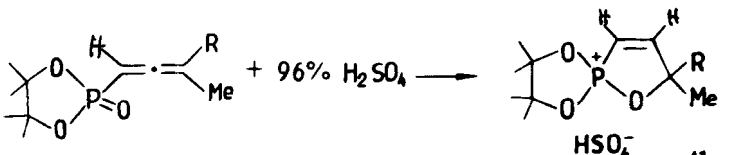
40	R	R^1	R^2
a	Me	Me	Me
b	Ph	OMe	Me
c	OMe	OMe	Me
d	OPr-i	OPr-i	Me
e	OMe	OMe	Et

X = Cl^-, HSO_4^-, CF_3COO^-

Y = Cl^-, HSO_4^-, OH^-, H_2O

From the equation it can be seen that in acidic medium the existance of quasiphosphonium salts is established which is a direct confirmation of the assumption that the reaction of these phosphonates with halogens, sulfenyl chlorides and hydrogen chloride in the intermediate stage proceeds through such cyclic structures.

Recently it was established that during protophilic cyclization in 96% H_2SO_4, the allene-containing 2-oxo-1,3,2-dioxaphospholanes are forming spiro-phosphonium salts **41**:[56]



Scheme 16

IV. CONCLUSION

The experimental results discussed in this review do not include all the possibilities for interaction of allene organophosphorus compounds with electrophilic reagents. However, they allow some conclusions to be made, concerning the reaction route. In the first place, the direction of the reaction depends, essentially, on the structure of the phosphorylated allenes. It is shown that the oxaphospholene cyclization of the 1,2-propadienylphosphonic derivatives proceeds with small probability. For 1- or 3-monosubstituted allenylphosphonates dependent upon the nature of the electrophile, the reaction proceeds with formation of cyclic compounds; further reaction of these produces 1,2-adducts. 3,3-Disubstituted phosphorylated allenes, with few exceptions, lead to the formation of 1,2-oxaphosphol-3-ene derivatives. The differences mentioned above show that cyclization of the substituted allenes is preferred. This is an indication for the important role of the substituents at the allenic bond for the stabilization of the transition state of the reaction. Secondly, the essential features of the behavior of the sulfenyl chlorides in the reaction with alkatrienyl phosphonic esters can be explained with the ability of sulfur to form relatively stable episulfonium ions, which are not strongly influenced by electronic factors. The existence of such ions has been postulated repeatedly for other unsaturated compounds.[57-59] These features lead to the discovery of heterocyclization with formation of the thiophene ring system, a reaction previously unknown in the field of organophosphorus chemistry. Thirdly, the conditions under which the reactions are carried out also influence the oxaphospholene cyclization. Very frequently they can be chosen in such a way that the reaction proceeds in the desired direction.

Further investigations on the interaction of phosphorus containing allenes with electrophiles undoubtedly will enrich the present review with new facts and will enable the detailed mechanistic features of the chemical transformations of phosphorylated allenes in these reactions to be determined.

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