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Phosphorylated allenes: structure and interaction with electrophiles

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Abstract. Data on the structures of phosphorylated allenes (PA) and their reactions with electrophiles are surveyed for the first time. It is shown that the influence of intramolecular interactions on the reactivity of the unsaturated centres is reflected in the selectivity of the reactions of PA with electrophiles. Depending on the nature of the reactants and the structure of the PA, various reaction mechanisms may operate. The bibliography includes 163 references.

I. Introduction

The unusual system comprising interlinked unsaturated centres, differing in properties and reactivity, in molecules of phosphorylated allenes (PA) as well as the ready availability of these compounds and the wide variety of chemical reactions based on them have long attracted the attention of chemists (see, for example, Refs 1 – 4). Vigorous studies on PA are also being continued at the present time. The results obtained in recent years have appreciably altered and amplified the general ideas concerning the compounds of this class. Firstly, the range of synthetic reactions based on PA has expanded significantly and it became necessary to refine the concept of their reactivity. Secondly, it was in fact in recent years that the structures of certain PA were first investigated by X-ray diffraction methods (in the case of crystalline substances) and by gas electron diffraction (in the gas phase). In addition, the quantum-chemical calculations which have been carried out (both by semiempirical and *ab initio* methods) together with photoelectron spectroscopic data made it possible to characterise fairly reliably for the first time the electronic structure of PA. In connection with the growing interest in the synthesis of promising physiologically active substances [5 – 17] from PA, a systematic treatment and combined analysis of the experimental data accumulated were required. The present review surveys the new data on the structure of PA and their interaction with electrophiles.

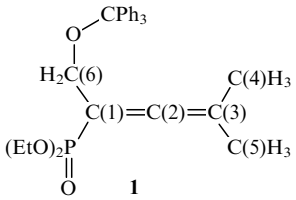
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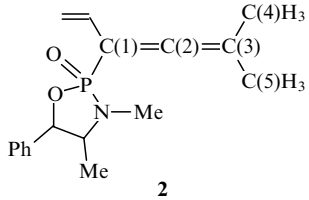
II. Characteristic features of the structure of phosphorylated allenes

The mutual influence of three fragments — two mutually orthogonal double bonds and the phosphoryl group — in PA molecules can be exerted both *via* bonds and through space [18 – 20] and can alter the properties and reactivity of these isolated fragments.

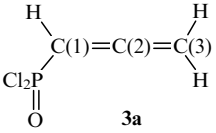
Up to the beginning of the 1990s, the structures of PA had not been investigated and studies [21, 22] on the X-ray diffraction of the allenic phosphonate **1** and the allenic 1,3,2-oxazaphospholidine **2** as well as the report [23] concerning the investigation of the dichlorides of allenylphosphonic acid **3a** and 3-methylbuta-1,2-dienylphosphonic acid **3b** by gas electron diffraction (GE) were published only a few years ago. The geometrical parameters of the principal fragments of molecules of compounds **1 – 3a**,**b** are presented in Table 1.



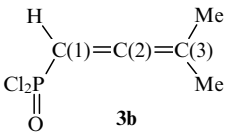
1



2



3a



3b

The allene fragment in PA molecules is linear and has an orthogonal configuration of the substituents at the C(1) and C(3) atoms. The C(1) = C(2) bond is somewhat longer than the double bond remote from the phosphorus atom. The lengths of both bonds are close to the value 1.3129(9) Å obtained [24] for propadiene $CH_2=C=CH_2$.

The lengths of the P – Cl bonds in the molecules of the dichlorides **3a**,**b** [2.011(1) and 2.024(2) Å respectively] are close to the values found for vinylphosphonic dichloride $CH_2=CH-P(O)Cl_2$ [2.016(4) Å][25] and methylphosphonic dichloride $MeP(O)Cl_2$ (2.011 – 2.013 Å)[26] and are somewhat greater compared with the analogous bonds in the $POCl_3$ molecule [1.992(3) Å]. The P = O (1.453 Å) and P – O (1.566 – 1.574 Å) bonds in the molecule of the allene **1** have lengths almost identical with the statistical average values for the $(XO)_2P(O)-C$ fragments 1.457(9) Å for P = O and 1.571(13) Å for P – O.[27]

In the molecules of the allenes **1** and **3a**, which are predominantly (100% and 72% respectively) in the *s-cis*-conformation

Table 1. The bond lengths (d) and O=P–C=C torsional angles (φ) in the molecules of the PA **1**–**3a**,**b**.

Compound	Method	d/Å				φ/deg
		C(1)–C(2)	C(2)–C(3)	C(1)–P	P=O	
1	XRD	1.316(3)	1.308(3)	1.787(2)	1.453(2)	0
2	XRD	1.311(3)	1.307(4)	1.812(2)	1.465(2)	130
3a	GE	1.318(4)	1.318(4)	1.795(3)	1.461(3)	0 (72.1%)[a] 123 (27.9%)[a]
3b	GE	1.307(7)	1.307(7)	1.804(9)	1.451(7)	0 (51.6%)[a] 109.1 (48.4%)[a]

[a] The fraction of the corresponding conformation.

(the O=P–C=C torsional angle is $\varphi = 0$ °), the P–C(1) bond is somewhat shorter compared with the statistical average length of the P–C(sp^2) bond, which is 1.81 Å [26,28–30] (1.817–1.822 Å for the dichloride of vinylphosphonic acid); in the case of the allene **3b** (51.6% of the *s-cis*-conformation), this effect is weaker; in the molecule of compound **2**, where the O(1)=P–C(1)=C(6) fragment has the anticlinal conformation, the P–C(1) bond length is close to the standard value. This suggests either a comparatively lower degree of conjugation in the molecules of *s-cis*-PA or the occurrence of a different, specific to allenylphosphonates, intramolecular interaction in the case of the *s-cis*-conformation. This question will be considered below; we shall only note that the interaction through space of the 3*d* orbitals of the P atom with the π-system of the allyl double bond, mentioned previously, is impossible for PA because of considerations relating to the molecular geometry.[31]

The conformational composition of the PA has been investigated with the aid of vibrational spectroscopy (IR and Raman),[32–35] the dipole moment method,[36,37] the Kerr effect,[36] and electron diffraction in the gas phase.[23] The results of all the investigations show that the principal conformation relative to the C–P bond is cisoid, characterised by the coplanar disposition of the O=P–C=C fragment ($\varphi \approx 0°$). The fraction of this conformation varies as follows: 72% in the gas phase [23] and 70% in solution [37] for the allene **3a**, 51.6% in the gas phase [23] for the phosphonic dichloride **3b**, and 100% in the crystalline state for compounds **1** and **3a**,**b** and a number of other allenes [21,37] (with the exception of compound **2**).[22] Our calculation of the dependence of the total energy of the allene **3a** molecule on the O=P–C(1)=C(2) angle by the PM3 method demonstrated the presence of two minima — a deeper minimum corresponding to the *cis*-conformation ($\varphi = 0$ °) and a shallow minimum at 180 °. The rotational barrier is < 2 kcal mol^{-1}. These results agree with the literature data on the conformational equilibrium in the allenecarboxylic [38] and vinylphosphonic acids,[35,39–41] for which the eclipsed conformation is also the most stable.

At the same time, it is essential to note that ideas concerning the geometry of the second conformer of PA (as well as vinylphosphonates) have changed in recent years. It had been postulated earlier that the minor component is characterised by planar *s-trans*-dispositions of the atoms of the O=P–C=C fragment (by analogy with acrylic acid derivatives [42]). However, the results of recent studies on PA by gas electron diffraction [23] support a nonplanar structure of this fragment. Thus, in the case of the allenes **3a**,**b**, a mixture of two rotational isomers with the following angle φ corresponds to experimental data: 0 ° (72.1%) and 123.3 ° (27.9%); 0 ° (51.6%) and 109.1 ° (48.4%). The anticlinal conformation (130 °) occurs also for the allene **2** in the crystalline state.

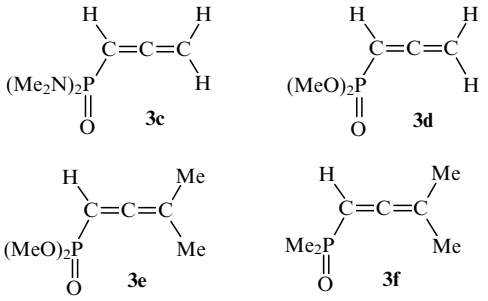
Analysis of vibrational spectra [35] and *ab initio* calculations [43–45] led to similar results as regards the conformational equilibrium in the molecules of vinyl- and *trans*-propenyl-phosphonates: the second minimum corresponds to the anticlinal conformation (the planar *s-trans*-conformation corresponds to the transition state) for rotational barriers of ~3 kcal mol^{-1}. For the conformers of *cis*-propenyl-phosphonates, the barriers to internal rotation are much higher. The fraction of the *s-trans*-form increases with increase in the steric hindrance induced by the interaction of the phosphoryl group and the substituent in the *cis*-position and also with increase in solvent polarity.[46] The total energy minimum at $\varphi = 0$ ° is due to the interaction of the nonbonded atoms, while the additional minimum is caused by intramolecular charge transfer from the vinyl fragment to the phosphorus-containing group.[47]

The question of the existence and extent of conjugation in PA molecules arises in connection with the nonplanar structure of the minor conformers. Since there is virtually no information about this in the literature, we shall consider briefly data on conjugation in vinylphosphonic acid derivatives, assuming that the general rules are valid also for PA. It has been noted [35] that the extinction coefficients of vinylphosphonates are higher than those of the homologous allylphosphonates. This indicates the presence of π-conjugation between the vinyl and phosphorus-containing fragments, but it is much weaker than, for example, in the case of acrylic acid derivatives. The absorption by propenylphosphonates is greater than by vinylphosphonates, which may be accounted for by the hyperconjugation effect of the methyl group. The negative charge on the C(1) atom of vinylphosphonic acid is higher than on the C(2) atom (Table 2). This finding was initially regarded as an argument in support of the conjugation of the double bond and the P=O group,[43] but it was shown later [44,45] that in this system conjugation is manifested weakly and that the inductive effect and hyperconjugation with participation of the PO_3 fragment must be invoked in order to account for the electronic structure of vinylphosphonates. The strong π-acceptor effect of the O=PCl_2 fragment has been attributed [48] to the group π* orbitals made up of the σ* orbitals of the P–Cl bonds.

The structure of the PA **3a**–**f** has been investigated by photoelectron (PE) spectroscopy and by means of quantum-chemical nonempirical calculations.[49] It was shown that the 4-31 G basis set is the minimal basis set for the establishment of proportionality between the calculated molecular orbital (MO) energies and the experimental ionisation potentials (IP).

Table 2. The effective charges (q) on the carbon atoms of allene and ethene derivatives (calculated *ab initio* in terms of the 4-31 G basis set).

Compound	q/e		
	C(1)	C(2)	C(3)
$H_2C(1)=C(2)=C(3)H_2$ **8**	−0.380	−0.008	−0.380
$H_2C(1)=C(2)=C(3)Me_2$ **7**	−0.360	−0.042	−0.008
$H_2PC(1)H=C(2)=C(3)H_2$ (O) **9**	−0.663	0.135	−0.337
$H_2PC(1)H=C(2)=C(3)Me$ (O) **10**	−0.653	0.103	−0.008
$Cl_2PC(1)H=C(2)=C(3)H_2$ (O) **3a**	−0.585	0.156	−0.332
$Cl_2PC(1)H=C(2)H_2$ (O) **4**	− 0.496	−0.214	–
$Cl_2PC(1)H=C(2)H_2$ (S)	−0.432	−0.225	–



According to *ab initio* calculations, the main contribution to the highest occupied MO comes from the $p\pi$(O) and the π_1 and π_2 orbitals of PA [$\pi_1(a'')$ is the orbital of the C atom closest to the P atom and $\pi_2(a')$ is the orbital of the C atom remote from the P atom; a' and a'' correspond to the symmetry and antisymmetry of these orbitals relative to the OPCC reflection plane respectively]. The ionisation energies are similar and vary as a function of the nature of the substituents at the C atom. Fig. 1 presents the correlation diagram for the ionisation potentials of a series of PA, the dichloride of vinylphosphonic acid **4**,[49] its diethyl ester **5**,[47] and the bis(dimethylamide) **6**,[50] 3-methylbuta-1,2-diene **7**, and propadiene **8**.[51] The form and intensity of the bands in the PE spectra of PA permit the interpretation, to a first approximation, of the experimental IP as the ionisation energies of individual fragments of the molecule. We shall consider how the mutual influence of these fragments affects the ionisation potentials of PA.

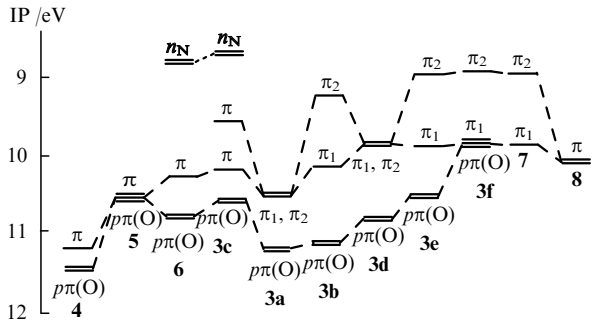


Figure 1. The correlation diagram for the ionisation potentials of the phosphorylated allenes **3a**–**f**, the alkenes **4**–**6**, 3-methylbuta-1,2-diene **7**, and propadiene **8**.

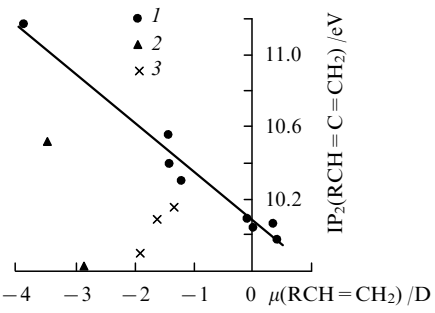


Figure 2. The correlation of group dipole moments (μ) of the substituents and the second ionisation potentials of allenes (*1*), PA (*2*), and alkoxyallenes (*3*).

The replacement of two H atoms in the dichloride of vinylphosphonic acid by the methylene fragment increases the energy of the C(1) = C(2) bond by 0.7 eV, compensating fully the decrease in the energy of the corresponding π orbital caused by the presence of the electron-accepting $O=PCl_2$ fragment (IP_1 for ethene is 10.51 eV [52]), while the introduction of the $=CMe_2$ fragment increases the energy of the C(1) = C(2) bond by 1 eV. On passing from ethene to allene, the energy of the π orbital increases by only 0.5 eV. Comparison of the data for PA with the analogous values for a series of other allenes [53] shows that the influence of the phosphorus-containing fragment on the π_1 bond is considerable and is largely determined by the inductive effect of the substituent. The transfer of electron density from the allene system to the phosphoryl group explains the decrease in the ionisation energy of the $p\pi$(O) orbital on passing from the dichloride of vinylphosphonic acid **4** (11.5 eV) to the dichloride of allenylphosphonic acid **3a** (11.25 eV); the ionisation energy of the $p\pi$(O) orbital of the allene **3b** disubstituted at the C(3) atom (11.14 eV) is lower still. We quote for comparison the known ionisation energies of the $p\pi$(O) orbitals for $(EtO)_2P(O)H$ (11.35 eV), $(EtO)_2P(O)NEt_2$ (11.41 eV),[54] and $Cl_2P(O)Me$ (11.49 eV).[55] On the other hand, the ionisation energies of the $p\pi$(O) orbitals of diethyl vinylphosphonate **5** and the allenylphosphonic acid derivatives **3c**,**d** were found to be similar, the IP of the allene **3d** being higher than that of the phosphonate **5** (10.7 and 10.6 eV respectively).

The replacement of two H atoms in the ethene molecule by the $Cl_2(O)P-C=$ fragment hardly influences the ionisation energy of the double bond (10.5 eV), while IP_2 of the allene **3b** is higher than the ionisation energy of the π orbital of isobutene (9.24 eV)[52] by only 0.17 eV. Furthermore, the ionisation energy of the π orbitals of the phosphonate **3d** was found to be lower than that for the unsubstituted allene $H_2C=C=CH_2$ (10.04 eV). It had been shown earlier that the influence of the substituent on the bond of the allene system remote from it is best described within the framework of the long-range field effect, whereupon there is a correlation between the IP of monosubstituted allenes and the dipole moments of the corresponding alkenes.[53] It might have been expected that the introduction of a phosphorus-containing fragment would appreciably reduce the energy of the π_2 orbital and the corresponding IP of the allene **3a** would therefore be higher by 0.5 eV than the observed value (Fig. 2) For the allene **3d**, the difference between the real ionisation potential and the value expected on the basis of the inductive effect approaches 1 eV. The validity of the employment of this correlation for PA is based on the similar conformational behaviour of PA and vinylphosphonates and also on the existence of the above correlation for the π_1 orbitals. A similar albeit a weaker effect (Fig. 2) has been observed in the series of alkoxyallenes $(RO)HC=C=CH_2$.[56] It can be explained by the orbital interaction of the nonbonded fragments through space.

Quantum-chemical calculations of the molecular orbital energies of a series of PA by the AM1 and PM3 methods have indicated the possibility of orbital interactions specific to allene derivatives of phosphonic acids in the *s-cis*-conformation, namely, the interaction through space of the P(O) orbital of the oxygen atom of the O = P group with the π_2 orbital in the allene system having a similar energy and symmetry (Fig. 3). The effectiveness of this interaction should increase with decrease in the difference between the energies of the π_2 and p(O) orbitals and hence should be manifested most strongly in the molecules of allenylphosphonic acid amides and allenylphosphine oxides. As a result of this, the *s-cis*-conformers of the latter should be additionally destabilised. The two mutually orthogonal π systems comprising the PA skeleton (the O = P group may be regarded as a highly polarised triple bond [57]) are analogous to the system of two triple bonds.[19] For PA conformations other than the *s-cis*-form, account must be taken of the possibility of similar orbital interactions through space with participation of, for example, the lone pairs of the O atom in the POC fragment, *etc*.

Thus the mutual influence of the phosphorus-containing fragment and the double bond remote from the P atom is manifested by two mutually compensating effects, which determines the unique position of PA both in the series of other

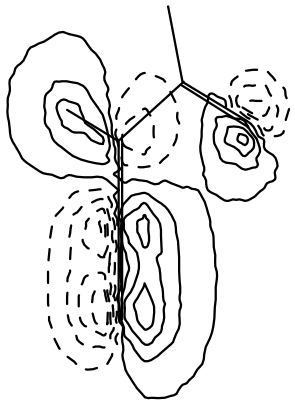


Figure 3. The highest occupied MO of the allene **3** (calculation by the PM3 method; the continuous and dashed lines correspond to different signs of the wave function).

unsaturated phosphoryl compounds and in the series of substituted allenes.

We shall consider in greater detail the changes in the allene system occurring when the substituents at the P atom are varied. The presence of the $X_2P=O$ (X = Me, OMe, Cl) group has little effect on the relative energies of the π_1 and π_2 orbitals: the energies of the latter in the molecules of compounds **3a** and **3d** are similar, whilst for the allenes **3b**, **3e**, and **3f** the difference between them is equal to the difference between the energies of these orbitals in the molecule of 3-methylbuta-1,2-diene **7**. The absolute energies of the π_1 and π_2 orbitals in the molecules of compounds **3e**,**f** and **7** are similar; in the presence of the more electron-accepting $Cl_2P=O$ group, they diminish by approximately 0.5 eV. On the other hand, in the molecule of the dimethylamide **3c** the energies of the π orbitals differ appreciably and there exists qualitative evidence supporting the assignment of IP_2 (9.56 eV) to the π_1 orbital. The presence of two methyl groups at the P atom in the phosphine oxide **3f** greatly reduces the ionisation energy for the O=P group.

Table 2 presents the effective charges on the atoms of the allene fragment calculated *ab initio* in terms of the 4-31 G basis set,[49] while Table 3 presents data on the energies and compositions of the π orbitals of the two model PA **9** and **10**, the acid chloride **3a**, and the dienes **7** and **8**. Similar data have been obtained [1, 58] with the aid of the semiempirical CNDO/2 method (the *spd* basis set). The degenerate frontier orbitals of the unsubstituted allene are located predominantly on the terminal atoms. The presence of the $H_2P=O$ or $Cl_2P=O$ group in the allene molecule has little effect on the relative energies of the π orbitals, but leads to a slight delocalisation of the latter and also to a change in the polarisation of the π_1 bond. The situation changes sharply in the case of the allenes **3b**,**e**,**f** in which the degeneracy of the π orbitals is removed as a consequence of hyperconjugation with the methyl groups; the polarisation of the π_2 orbital then changes and the overall electron density on the C(3) atom is appreciably reduced.

The calculated atomic charges are satisfactorily correlated with ^{13}C NMR spectroscopic data (Table 4) and illustrate the influence of the substituents on the distribution of electron density in PA molecules. The change in the polarisation of the π_1 bond on passing from 3-methylbuta-1,2-diene to PA is manifested by a downfield shift of the C(1) signal. The presence of alkyl substituents at the C(3) atom leads to a 10–15 ppm downfield shift of its signal in the ^{13}C NMR spectrum.[59] The chemical shifts in the ^{31}P and ^{1}H NMR spectra of PA are in the usual range for unsaturated phosphonic acid derivatives and have been discussed in fair detail.[1]

The dipole moments of PA are somewhat greater compared with those of the corresponding alkenylphosphonic and alkadienylphosphonic acid derivatives [36] (Table 5), the experimental values exceeding the values calculated assuming additivity. This

Table 3. The energies (E_m) and populations of the π orbitals (q_m) of a series of PA.

Compound	MO	E_m	π_2[C(1)=C(2)]		π_2[C(2)=C(3)]	
			$q_m^{z,1}$	$q_m^{z,2}$	$q_m^{x,2}$	$q_m^{x,3}$
8	ψ_1^*	4.92	0.507	0.462	–	–
	ψ_1	−10.04	0.212	0.163	–	–
	ψ_2^*	4.92	–	–	0.462	0.507
	ψ_2	−10.04	–	–	0.163	0.212
7	ψ_2^*	5.17	0.506	0.478	–	–
	ψ_2	−9.89	0.262	0.205	–	–
	ψ_1^*	4.98	–	–	0.403	0.373
	ψ_1	−9.25	–	–	0.216	0.218
9	ψ_1^*	3.42	0.359	0.504	–	–
	ψ_2	−10.72	0.186	0.120	–	–
	ψ_2^*	3.56	–	–	0.339	0.432
	ψ_1	−10.46	–	–	0.174	0.193
10	ψ_1^*	3.84	0.323	0.504	–	–
	ψ_2	−10.42	0.211	0.130	–	–
	ψ_2^*	3.97	–	–	0.269	0.390
	ψ_1	−9.61	–	–	0.231	0.186
3a	ψ_2^*	2.53	0.208	0.421	–	–
	ψ_2	−11.65	0.267	0.152	–	–
	ψ_1^*	2.27	–	–	0.108	0.193
	ψ_1	−11.24	–	–	0.231	0.186

has been attributed [36] to the increased polarisability of the allene system under the influence of substituents, which confirms the transfer of electron density from the allene system to the phosphorus-containing fragment. The dipole moments of PA with identical structure of the allene skeleton increase in the following sequence: esters < acid dichlorides < dimethylphos-phine oxides. The dipole moments of allenes mono- and di-substituted at the C(3) atom are somewhat higher.

The molecular electrostatic potential (EP) is used widely to determine the interaction energies in the initial stage of the reaction and the direction of attack on the substrate by charged species.[60] This quantity is relatively insensitive to the accuracy of the wave functions and the results of calculations by semiempirical methods are comparable to those of *ab initio* calculations.[61]

Photoelectron spectroscopy makes it possible to obtain objective information about occupied molecular orbitals.[62] There are at present no experimental data on this topic. We shall therefore henceforth make use exclusively of the results of quantum-chemical calculations (Table 2).[49] The first and second unoccupied molecular orbitals of PA are located on one of the double bonds of the allene system. According to *ab initio* calculations in terms of the 4-31 G basis set, the energy of the π_2^* orbital in molecules of the allenes **9** and **10** is lower than that of the π_1^* orbital. The introduction of two Cl atoms into the phosphorus-containing fragment decreases the energies of both lowest unoccupied orbitals in compound **3a**, the influence on the π_2^* orbital being greater. This leads to the inversion of the unoccupied orbitals, but the difference between the energies of the π_1^* and π_2^* orbitals remains small. On the other hand, the population of the $2p\pi$ atomic orbitals of the C(1)=C(2) bond exceeds by a factor of 2 the degree of localisation of the π_2^* orbital of the C(2)=C(3) bond and according to Zverev *et al.*,[49] this particular orbital actually controls the interaction of the allene **3a** with aryl azides. The AM1 method yields results qualitatively close to the values calculated by the *ab initio* method, although it leads to the inversion of the unoccupied orbitals for the allene **3a**.

According to the calculation in terms of the 4-31 G basis set, the energies of the unoccupied and occupied π and π^* orbitals in the molecules of PA vary in parallel. This made it possible to

Table 4. Chemical shifts (δ) in the ^{13}C NMR spectra of PA and related compounds.

Compound	δ /ppm			Ref.	Compound	δ /ppm			Ref.
	C(1)	C(2)	C(3)			C(1)	C(2)	C(3)	
$H_2C(1)=C(2)=C(3)Me_2$	72.1	207.5	93.1	58	$HOPHC(1)H=C(2)=C(3)H_2$ (O)	92.4	217.5	85.9	58
$Cl_2PC(1)H=C(2)=C(3)H_2$ (O)	89.7 (90.0)	212.1 (212.9)	79.3 (80.5)	58 59	$HOPHC(1)H=C(2)=C(3)Me_2$ (O)	80.8	211.3	99.8	58
$F_2PC(1)H=C(2)=C(3)H_2$ (O)	80.9	217.3	78.3	58	$(HO)_2PC(1)H=C(2)H_2$ (O)	129.59	136.67	–	35
$(EtO)_2PC(1)H=C(2)=C(3)H_2$ (O)	79.8	218.6	75.8	58	$(MeO)_2PC(1)H=C(2)=C(3)Me_2$ (O)	75.1	209.9	96.0	59
$(EtO)_2P(O)-C(1)(Me)=C(2)=C(3)H_2$	88.7	216.0	75.7	58	$(HO)_2PC(1)H=C(2)=C(3)Me_2$ (O)	80.8	211.3	99.8	59
$(MeO)_2PC(1)H=C(2)=C(3)H_2$ (O)	77.4	215.5	96.8	58	$(MeO)_2PC(1)H=C(2)=C(3)(CH_2)_5$ (O)	73.7	205.6	101.2	59
$Cl_2PC(1)H=C(2)=C(3)Me_2$ (O)	89.4	209.3	103.8	58	$(MeO)_2P(O)-C(1)(Bu^t)=C(2)=C(3)Me_2$	100.1	206.1	97.1	59
$Me_2PC(1)H=C(2)=C(3)Me_2$ (O)	85.4	207.5	96.5	58	$(MeO)_2P(O)-C(1)(Bu^t)=C(2)=C(3)HBu^t$	104.4	205.4	104.4	59

Table 5. The dipole moments (μ) of a series of PA.

Compound	μ /D	Ref.
$H_2C=C=CHP(O)(OMe)_2$	3.01	37
$H_2C=C=CHP(O)(OEt)_2$	3.14	36
$H_2C=C=CHP(O)Cl_2$	3.51	37
$H_2C=C(Me)-P(O)(OMe)_2$	3.14	36
$H_2C=C(Me)-P(O)(OEt)_2$	3.07	36
$MeCH=C=CHP(O)(OEt)_2$	3.32	36
$Me_2C=C=CHP(O)(OMe)_2$	3.46	36
$Me_2C=C=CHP(O)(OEt)_2$	3.38	36
$Me_2C=C=CHP(O)Cl_2$	4.20	37
$Me_2C=C=CHP(O)Me_2$	4.70	37
$(CH_2)_5C=C=CHP(O)(OMe)_2$	3.54	37
$(CH_2)_5C=C=CHP(O)(OEt)_2$	3.36	37
$(CH_2)_5C=C=CHP(O)Cl_2$	4.59	37

postulate [49] that, depending on the substituents at the P atom, the above compounds may behave as electron donors or acceptors or can interact *via* a neutral mechanism, as happens for example, in the reaction with aryl azides.[1] The characteristic features of the electronic structure of PA, responsible for their increased reactivity in relation to both nucleophiles and electrophiles, have attracted attention to PA as substrates for the investigation of biphilic reagents.

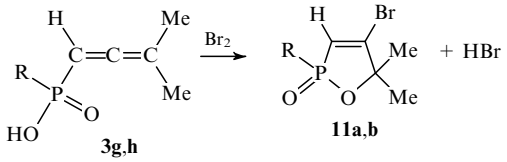
On the basis of the entire set of data examined above, one may postulate that, in contrast to allenes unsubstituted at the C(3) atom, the reactions of 3,3-disubstituted PA with electrophiles occur more readily and, in the case of orbital control,[63] selectively with respect to the C(2) = C(3) bond (HOMO). On the other hand, in the case of charge control electrophilic attack should be directed to the C(1) = C(2) bond, where the highest negative charge density is concentrated (Table 2).

Thus, by varying the substituents at the P atom and in the allene system, one may vary the reactivity of both the O atom of the phosphoryl group and of the two double bonds and, if required, one may activate selectively a particular reaction centre.

III. Interaction of phosphorylated allenes with electrophiles

1. Reactions of phosphorylated allenes with the halogens and sulfuryl chloride

In 1977, Braverman and Reisman [64] observed that allenylphosphinic and allenylphosphonic acids **3g**,**h** cyclise on treatment with bromine to 1,2-oxaphosphol-3-enes **11a**,**b** respectively.

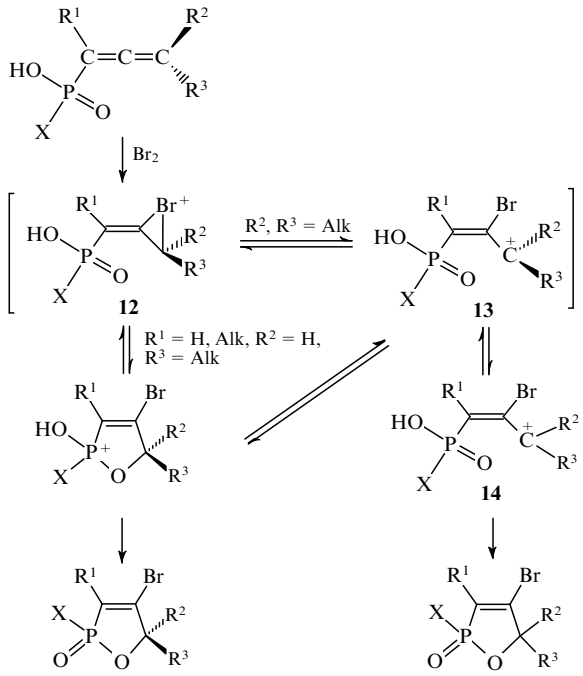


3g,**h** **11a**,**b**

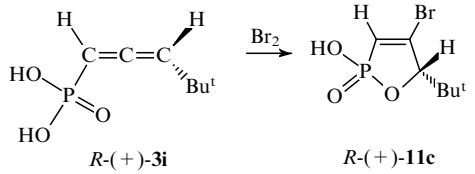
R = Ph (**3g**, **11a**), OH (**3h**, **11b**).

Subsequently it was shown that the bromination of PA monosubstituted at the C(3) atom is also accompanied by a similar cyclisation.[65]

Scheme 1



The intermediate formation of the tertiary carbonium ion **14**, in equilibrium with a quasi-phosphonium salt (Scheme 1), the elimination of HBr from which actually leads to the oxaphospholenes **11a**,**b**, has been postulated.[64] However, it has been shown [65] that the bromination of the optically pure acid **3i** takes place with 41% stereoselectivity. This shows that, in the case of allenylphosphonic acids monosubstituted at the C(3) atom, the bromonium ion **12** or the nonplanar secondary carbonium ion **13** is formed as an intermediate rather than the planar carbonium ion **14**. The O atom of the phosphorus-containing group (especially in the case of the *s-cis*-conformation) is capable of trapping the onium ion **12** fairly effectively, which prevents racemisation. The quasi-phosphonium salt formed is unstable and readily eliminates an HBr molecule. It is of interest to note that the bromination of optically active allenecarboxylic acids takes place with approximately the same stereoselectivity,[66] while in the case of the corresponding allenic alcohols complete racemisation is observed.[67]

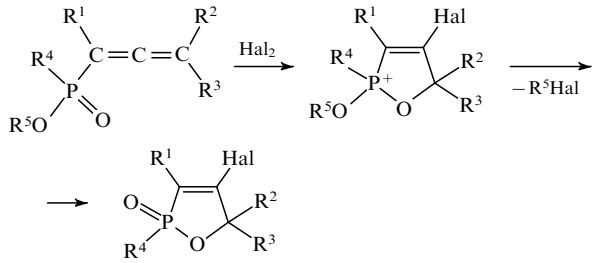


R-(+)-**3i** *R*-(+)-**11c**

The available information about the reactions of free alka-1,2-dienylphosphonic and the corresponding phosphonic acids with the halogens is limited to the two communications mentioned above. The halogenation of esters of these acids has been studied in greater detail.[64, 68–78] For substrates di- and mono-substituted at the C(3) atom, it is also as a rule accompanied by cyclisation (Scheme 2).

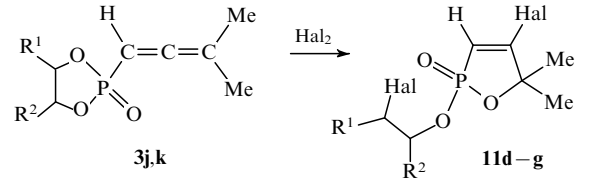
In this case, the reaction also proceeds *via* a stage involving the formation of insufficiently stable quasi-phosphonium salts, which rapidly split off an alkyl halide. The rate of the process depends on the nature of the halogen. On chlorination and bromination, cooling is required (the bromination reaction is weakly exothermic), while on iodination heating is needed. The reactivities of substituted allenylphosphonic esters in relation to interhalogens

Scheme 2



R^4 = Ph, R^5 = Alk; R^4 = R^5O, R^5 = Alk.

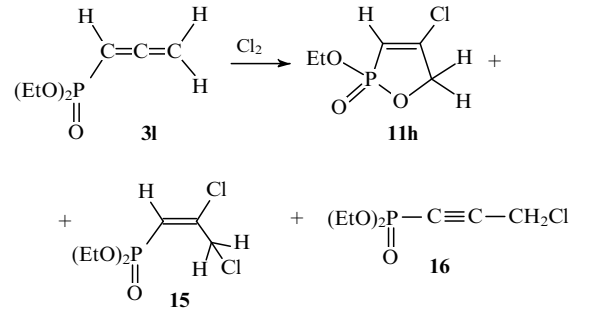
have been investigated [72] and it has been observed that the rate of reaction with ICl is almost twice as high as that with IBr (it is an order of magnitude higher than that for the reaction with I_2).



3j,**k** **11d–g**

R^1 = R^2 = H (**3j**, **11d**,**f**), Me (**3k**, **11e**,**g**); Hal = Cl (**11d**,**e**), Br (**11f**,**g**).

The halogenation of 2-oxo-1,3,2-dioxaphospholanes **3j**,**k** is accompanied by the opening of the dioxaphospholane ring and the formation of an oxaphospholene ring.[77] The oxaphospholene **11h** has been detected in a small amount on chlorination of diethyl propadienylphosphonate **3l**, although the main reaction products were found to be the 2,3-adduct **15** and diethyl propynylphosphinate **16**.[71]



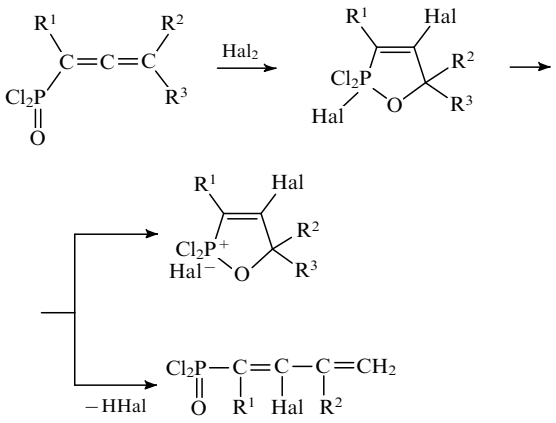
3l **11h** **15** **16**

The different ways in which 3-substituted allenylphosphonic and propadienylphosphonic acids are halogenated shows that the stability of the intermediate type **13** or **14** carbonium ion (see Scheme 1) is one of the decisive factors for the occurrence of cyclisation.

Sulfuryl chloride also reacts with the esters of di- and monosubstituted alka-1,2-dienylphosphonic acids with formation of 4-chloro-1,2-oxaphospholenes,[79, 80] while the reaction with propadienylphosphonic acid esters affords a complex mixture in which adducts formed *via* the C(2)=C(3) bond predominate.[80]

The mode of the halogenation reaction of allenylphosphonic acid dichlorides depends also on the substituents at the C(3) atom of the allene system. In the case of disubstituted allenes, tetrahalo-1,2-oxaphosphol-3-enes or quasi-phosphonium salts are formed.[81–90] The tetrahalo-1,2-oxaphosphol-3-enes are stable in nonpolar solvents for several days. After more prolonged storage, they split off the hydrogen halide and are converted into the dichlorides of the corresponding 2-haloalka-1,3-dienylphosphonic acids.[82, 84–91] A proton is split off from the least hydrogenated carbon atom in the substituents R^2 and R^3 (Scheme 3).

Scheme 3

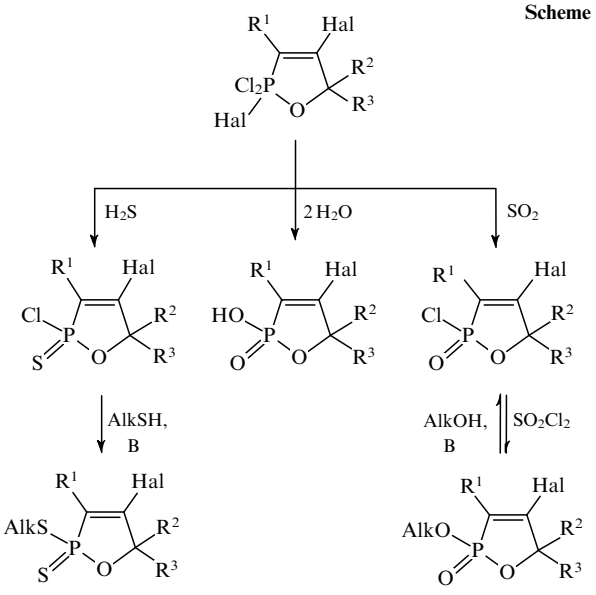


R^1 = H, Alk, Ar; R^2 = R^3 = Alk; Hal = Cl, Br.

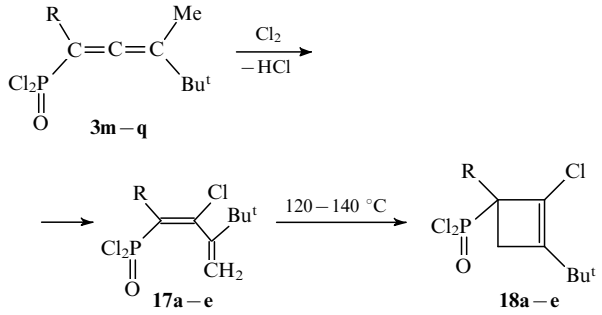
In polar solvents (such as nitromethane, chloroform, *etc.*), the evolution of the hydrogen halide is faster; it is accelerated on heating or removal of the solvent. The process is exothermic, *i.e.* the reaction proceeds in the direction of the thermodynamically more stable product. It is noteworthy that HBr is split off more readily than HCl and in certain cases the intermediate phosphorane cannot be detected. This may be explained by the fact that the bromo-derivatives of pentacoordinate phosphorus have a more polar structure.[82]

The properties of phosphoranes are characteristic of P^V halides. Thus they readily interact with various nucleophiles (Scheme 4).[83]

Scheme 4

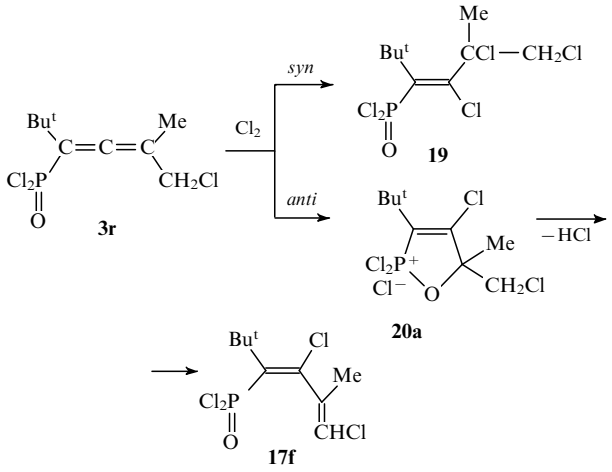


The alka-1,3-dienes formed from phosphoranes have the *s*-*cis*-configuration of the double bonds. This has been demonstrated by a study of their ^{1}H NMR spectra with the aid of lanthanide shift reagents[91] and also by studies of the configurations of the products of the reactions of dienes with electrophiles. The halogenation of the alka-1,3-dienylphosphonates obtained by the method described above is accompanied by cyclisation with formation of six-membered heterocycles — derivatives of 5,6-dihydro-2*H*-1,2-oxaphosphorine.[92,93] The halogenation of alka-1,3-dienylphosphonates synthesised by other methods (having the *s*-*trans*-conformation) leads not to oxaphosphorines but to the products of the addition of the halogen to the double bond remote from the P atom.[94] The skewed *s*-*cis*-conformation of the alka-1,3-diene system may impart also other unusual properties to phosphorus-containing alka-1,3-dienes. Thus, when the dichlorides of alka-1,3-dienylphosphonic acids **17a–e**, containing a bulky substituent in the 3-position, are heated, cyclisation takes place readily with formation of the dichlorides of cyclobutenylphosphonic acids **18a–e**.[95,96]



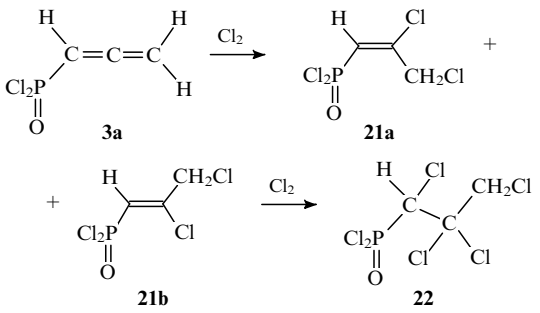
R = H (**3m**, **17a**, **18a**), $MeOCH_2$ (**3n**, **17b**, **18b**), $ClCH_2$ (**3o**, **17c**, **18c**), Ph (**3p**, **17d**, **18d**), *p*-MeC_6H_4 (**3q**, **17e**, **18e**).

The presence of a bulky group in the α-position relative to the P atom promotes an unusual mode of chlorination of the dichloride of 1-*tert*-butyl-4-chloro-3-methylbuta-1,2-dienylphosphonic acid **3r**: the adduct **19**, obtained by addition to the 2,3-double bond, is formed in 42% yield.[89,90]

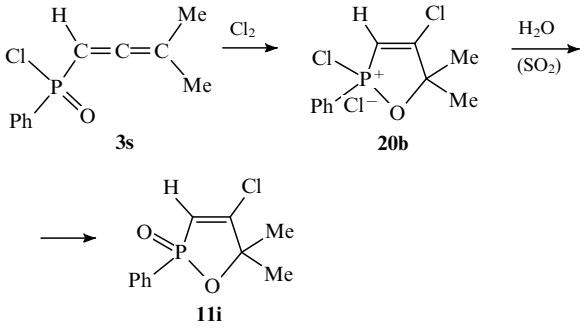


Evidently the presence of this compound can be accounted for by the *syn*-attack by the electrophile relative to the phosphorus atom — a process which is unfavourable in the majority of cases, but in this substrate is caused by the presence of the *tert*-butyl group. In addition, the phosphonium salt **20a** is formed in 39% yield. It is sufficiently stable to be isolated in a pure form. The salt structure of compound **20a** has been confirmed by the chemical shift of the phosphorus signal in the ^{31}P NMR spectrum: δ = +93 ppm.

The *syn*-attack by the electrophile takes place to a slight extent also on halogenation of the dichloride of propadienylphosphonic acid **3a**. It is noteworthy that the cyclisation is not observed also in the case of *anti*-attack relative to the phosphorus atom: this confirms yet again the decisive influence of the alkyl substituents at the C(3) atom on the direction of the process. The halogenation of the allene **3a** takes place only when the temperature is raised to 60–65 °C. One mole of Cl_2 adds to the double bond remote from the phosphorus atom with the predominant formation of a mixture of the dichlorides of 2,3-dichloro-1-(*E*)-propenylphosphonic acid **21a** and the corresponding *Z*-isomer **21b** (with the ratio 40 : 41 = 5 : 1). By carrying out the reaction at the same temperature for 8 h, it was possible to obtain the exhaustive chlorination product **22** in 72% yield.[71]

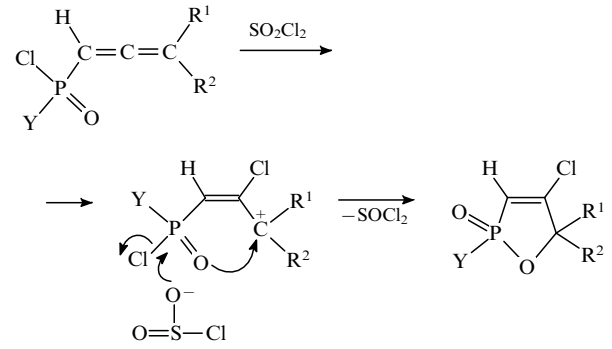


The chlorination of the chloride of 3-methylbuta-1,2-dienyl(phenyl)phosphinic acid **3s** leads to the formation of the phosphonium salt **20b**, which is converted into the oxaphospholene **11i** on interaction with moist air or SO_2. The same chain of reactions occurs on treatment with sulfuryl chloride.[97]



The use of sulfuryl chloride makes it possible to obtain derivatives of 1,2-oxaphosphol-3-ene from the dichlorides of alka-1,2-dienylphosphonic acids not only disubstituted but also monosubstitited at the C(3) atom.[79] The absence of alka-1,3-dienes of type **17a–e** in these reactions may be caused either by the rapid conversion of the intermediate phosphorane into an oxaphospholene with a tetracoordinate phosphorus atom as a result of the interaction with the SO_2 present in the mixture [79] or by the fact that the above phosphoranes are not formed at all as intermediates in the given instance. It has been suggested [2] that the reaction proceeds *via* a stage involving the formation of a carbonium ion with synchronous nucleophilic attack of the O atom of the phosphoryl group on the C(3) atom and of one of the O atoms of the sulfo-group on the P atom. This results in the elimination of the chloride ion and cyclisation (Scheme 5).

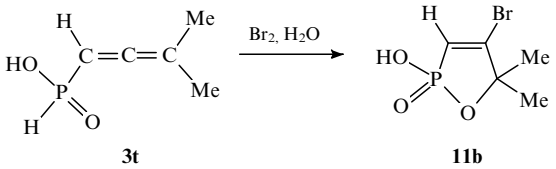
Scheme 5



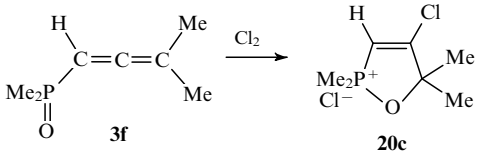
Y = Cl, Ph; $R^1 = R^2$ = Alk;
R^1 = H, R^2 = Alk.

The attack by Cl^- on the S atom leads to the elimination of thionyl chloride. The chloride of unsubstituted allenylphosphonic acid **3a** reacts with SO_2Cl_2 to form a complex mixture of adducts resulting from addition to the double bonds (as in chlorination by Cl_2).[71,79]

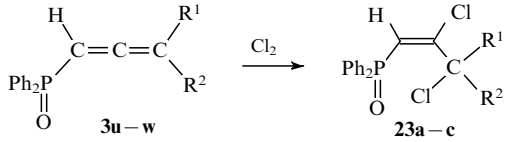
The modes of the reactions of PA with halogenating agents may depend not only on the substituents at the allene system but also on the nature of the groups at the P atom. Thus, in the interaction of 3-methylbuta-1,2-dienylphosphonous acid **3t** with bromine water, the cyclisation is accompanied by the oxidation of the P–H bond.[98]



The halogenation of the esters of alka-1,2-dienyl(phenyl)-phosphinic acid disubstituted at the C(3) atom leads to 1,2-oxaphospholenes.[64] In the reactions of allenylphosphine oxides with the halogens, cyclisation proceeds with formation of stable phosphonium salts, since in this case the stabilisation of the intermediate by the elimination of an alkyl halide is impossible. For example, the product of the reaction of the phosphine oxide **3f** with chlorine in CCl_4 is the cyclic phosphonium salt **20c**.[97]



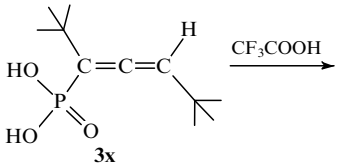
On the other hand, the diphenylphosphine oxides **3u–w** afford under the same conditions the products **23a–c**, which are 2,3-adducts. The observed differences may be explained by the fact that aromatic substituents, conjugated with the oxygen atom of the O=P group, reduce its nucleophilicity. However, according to Angelov *et al.*,[97] it is more likely that the bulky phenyl groups exert a steric influence on the geometry of the transition state, retarding cyclisation and promoting the addition reaction.

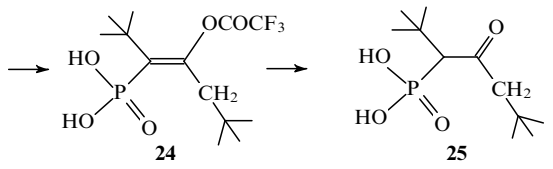


$R^1 = R^2$ = H (**3u**, **23a**), Me (**3v**, **23b**); R^1 = H, R^2 = Me (**3w**, **23c**).

2. Reactions of phosphorylated allenes with proton-donating electrophiles

The study of the reactions of alka-1,2-dienylphosphonic acids with Lewis acids [99,100] showed that only the acids disubstituted at the C(3) atom undergo protophilic cyclisation. Propadienylphosphonic acid affords exclusively decomposition products. 1,3-Di-(*tert*-butyl)allenylphosphonic acid **3x** does not interact with $HClO_4$ in tetrahydrofuran (THF) (18 h, 25 °C), with toluene-*p*-sulfonic acid in a $CHCl_3-H_2O$ mixture (54 h, 25 °C,),[101] and with 2 M HCl in 80% aqueous diglyme,[99] while the reaction with trifluoroacetic acid leads unexpectedly to the ketone **25** (in 85% yield).[100] This has been explained [100] by electrophilic attack on the terminal C atom of the allene system.

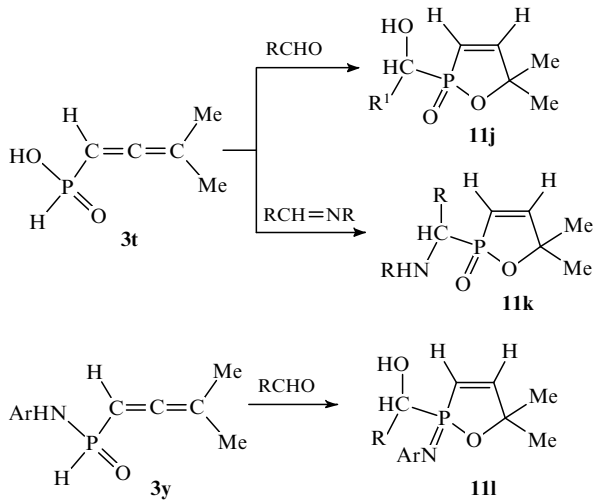




24 **25**

On interaction with carbonyl compounds[102, 103] and with azomethines,[103, 104] the acid **3t** cyclises *in situ* with formation of the 1,2-oxaphosphol-3-enes **11j**,**k** (Scheme 6). The analogous reaction of the corresponding amide **3y** with RCHO leads to the oxaphospholene **11l** containing the O–P=N fragment.[105]

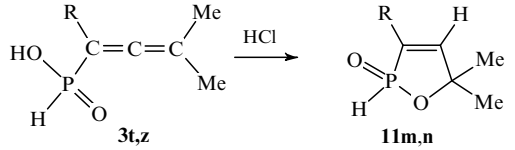
Scheme 6



3t **11j** **11k**

3y **11l**

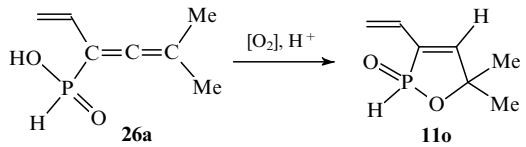
Treatment of 3,3-disubstituted alka-1,2-dienylphosphonous acids **3t**,**z** with gaseous HCl results in the formation of the oxaphospholenes **11m**,**n**.[106]



3t,z **11m,n**

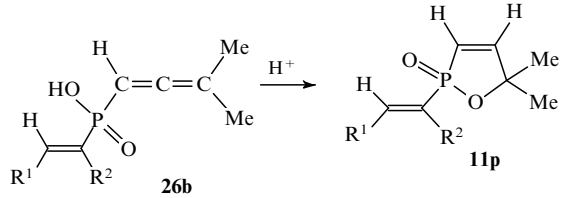
R = H (**3t**, **11m**), Me (**3z**, **11n**).

On treatment with HCl or hypophosphorous acids in the presence of atmospheric oxygen, hexa-1,3,4-trien-3-ylphosphonous acid **26a** cyclises, which is accompanied by the oxidation of the P–H bond.[107]



26a **11o**

Type **26b** phosphinic acids cyclise to oxaphospholenes above 100 °C in the presence of inorganic acids.[108]

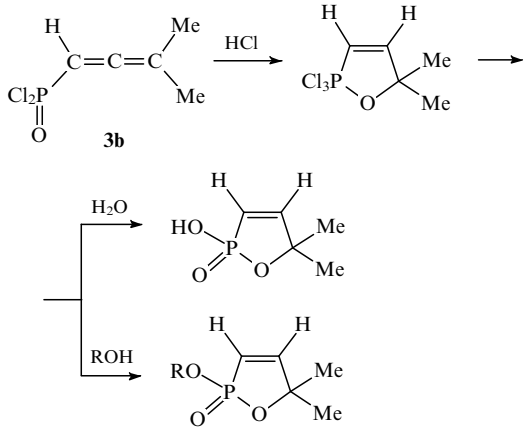


26b **11p**

R^1 = H, Br; R^2 = Ph, CH_2Br.

The dichlorides of alka-1,2-dienylphosphonic acids react very slowly with HCl (more slowly than with other electrophiles). After 24 h in inert solvents, the interaction of the chlorides of 3-monosubstituted and 3,3-disubstituted acids with HCl has not been observed.[109] This reaction could be achieved by keeping the mixture in CH_2Cl_2 for 25 days. In the case of the allene **3b**, it proceeds with formation of a cyclic phosphorane,[99] which, after treatment with water, affords the corresponding acid, while its interaction with alcohols gives rise to esters of this acid (Scheme 7).

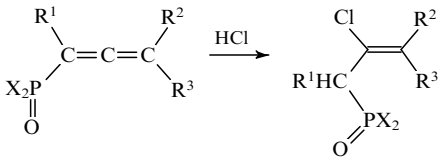
Scheme 7



3b

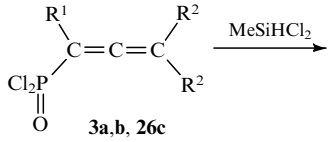
The hydrochlorination of the dichlorides of alka-1,2-dienylphosphonic acids is much faster in the presence of tertiary amines or other aprotic ionising additives, for example, the oxides of tertiary phosphines, hexamethylphosphoramide, *etc*.[76, 108] However, this reaction proceeds *via* a nucleophilic mechanism and leads to the dichlorides of 2-chloroalk-2-enylphosphonic acids. The corresponding acid difluorides react similarly (Scheme 8).[108] The presence of electron-accepting substituents promotes hydrocnlorination. Thus HCl adds to allenes containing the CH_2F group already during their synthesis from acetylenic alcohols and PCl_3 in the presence of pyridine while in the case where the CH_2Cl group is also present the reaction is so fast that the allene itself cannot be isolated.[76]

Scheme 8

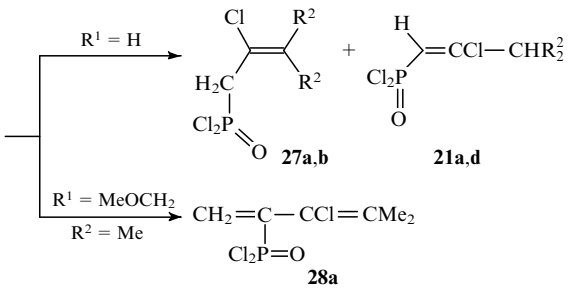


R^1, R^2, R^3 = Alk, Ar, CH_2Cl, CH_2F; X = Cl, F.

It has proved convenient to employ dichloromethylsilane for the hydrochlorination of the dichlorides of alka-1,2-dienylphosphonic acids **3a**,**b**. HCl then adds to the α- and β-double bonds.[110] The reaction of the dichlorides of 1-methoxyalka-2,3-diene-2-ylphosphonic acids **26c** with dichloromethylsilane leads exclusively to the product **28a** of the allene–1,3-diene isomerisation.[86]

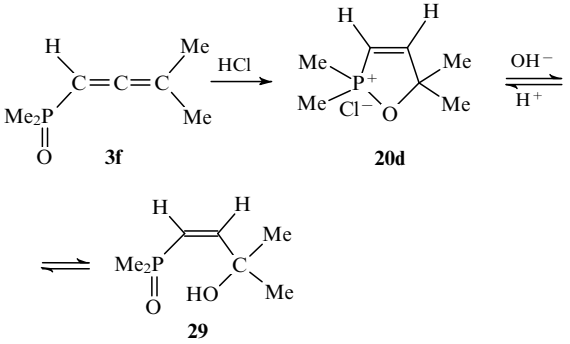


3a,**b**, **26c**



$R^1 = R^2 = H$ (**3a**, **27a**, **21a**,**b**);
$R^1 = H$, $R^2 = Me$ (**3b**, **27b**, **21c**,**d**);
$R^1 = MeOCH_2$, $R^2 = Me$ (**26c**, **28a**).

The hydrochlorination of PA having two or three P–C bonds is accompanied by cyclisation.[111] In the case of (3-methylbuta-1,2-dienyl)dimethylphosphine oxide **3f**, the quasi-phosphonium salt **20d** is formed. It is relatively stable in inert solvents,but is unstable in water and is in equilibrium with compound **29**. At pH 3, the equilibrium is fully displaced towards the open-chain compound. The ring opening may be regarded as the second stage of the Arbuzov reaction. In the given instance, the above process is reversible and the salt **20d** is reformed on raising the acidity to pH 1.



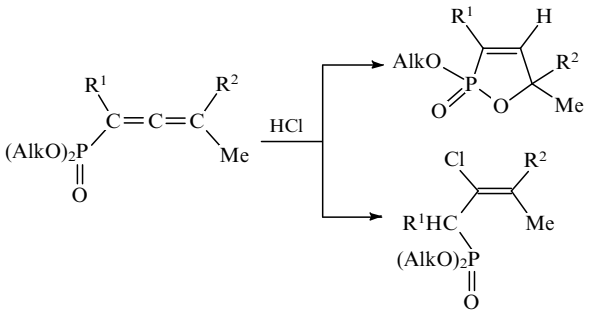
If concentrated H_2SO_4 is used for the cyclisation, it is possible to detect the formation of quasi-phosphonium salts also in the case of the esters of allenylphosphinic and allenylphosphonic acids.[111,112] On treatment with 40%–70% H_2SO_4 in water or aqueous dioxane, the hydrolysis of the quasi-phosphonium salts is so fast that they cannot be clearly detected. In both cases, the rate-limiting stage is the protonation of the allene to a carbonium ion, after which ring closure takes place with formation of a quasi-phosphonium salt.[111]

The influence of the acidity of the medium, of the isotope effect or the solvent, and of the structure of the phosphorus-containing compound on the rate and direction of the addition reaction has been investigated.[113] The rate constants obtained at different H_2SO_4 concentrations confirm that the reaction is acid-promoted. This is also indicated by the magnitude of the kinetic isotope effect k_H/k_D, which is 1.47 for 70% H_2SO_4 and 4.23 for anhydrous trifluoroacetic acid. Thus the cyclisation represents electrophilic addition involving a proton and the substrate in its rate-determining stage. It is noteworthy that the presence of the phosphorus-containing fragment in the substrate is responsible for certain differences from the majority of other reactions involving the conversion of an alkene into a carbonium ion.[113,114]

Depending on the nature of the substituent and the solvent polarity, the interaction of esters of 3,3-disubstituted alka-1,2-dienylphosphonic acids with HCl leads to the formation of 1,2-oxaphospholenes or 1,2-adducts (Scheme 9).[115,116]

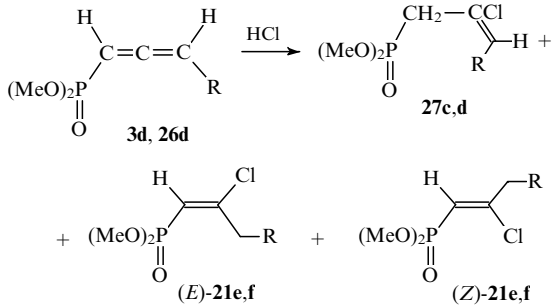
In polar solvents, cyclisation takes place exclusively. In non-polar solvents, the reaction proceeds in a more complex manner and 1,2-adducts are obtained together with 1,2-oxaphospholenes. The dimethyl esters of alka-1,2-dienylphosphonic acids, which

Scheme 9



afford only oxaphospholenes regardless of solvent polarity, are an exception. The phenyl substituent in the α-position in the allene system promotes partial hydrolysis of the ester to the corresponding cyclic acid.

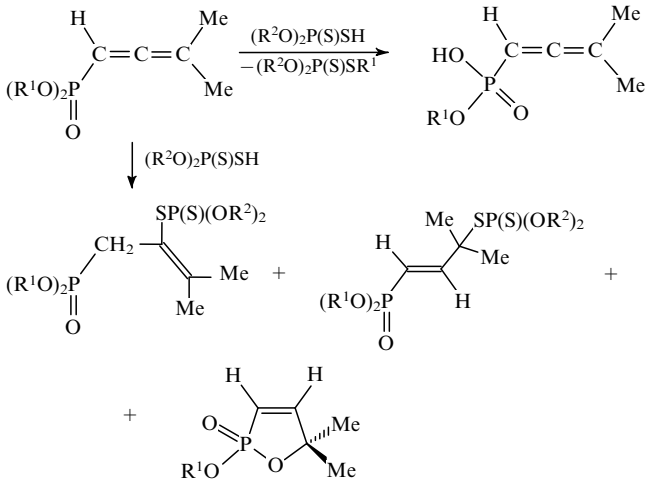
Unsubstituted alka-1,2-dienylphosphonates and the derivatives mono-substituted at the C(3) atom (compounds **3d**, **26d**) are not converted into oxaphospholenes even in polar solvents, giving rise to complex mixtures of products in which the adducts **27c**,**d** predominate.[65]



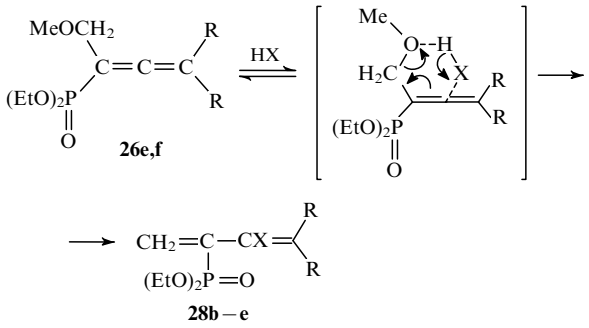
R = H [**3d**, **27c**, (*E*)-**21e**, (*Z*)-**21e**], Me [**26d**, **27d**, (*E*)-**21f**, (*Z*)-**21f**].

The interaction of PA with dithio-acids of phosphorus has been investigated.[117] Possessing dual reactivity, the acids can add to alkenes *via* both electrophilic and nucleophilic mechanisms. Apart from the products of the addition to the α,β-double bond of the allene (evidently *via* a nucleophilic mechanism) and of the alkylation of the dithio-acid by the alkoxy-group of the initial PA, small amounts of the β,γ-adducts (5%–7%) (Scheme 10) and (or) derivatives of 5,5-dimethyl-1,2-oxaphospholene (5%–6%) have also been detected in the reaction mixture. It is of interest that the 1,2-adducts are formed as a result of *syn*-attack relative to the phosphorus-containing fragment, whereas 1,2-oxaphospholenes are the products of *anti*-attack.

Scheme 10



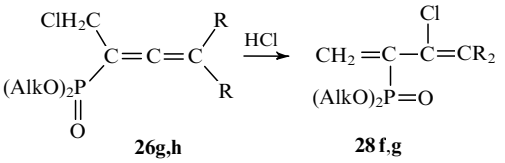
The introduction of functional groups makes it possible to expand still further the range of possible synthetic reactions of PA. The results of the hydrochlorination of 1-methoxybuta-2,3-dien-2-ylphosphonates **26e**,**f** proved of interest from this point of view.[118,119] The allene–diene rearrangement, accompanied by the elimination of an alkoxy-group, which results in the formation of 3-halobuta-1,3-dien-2-ylphosphonates **28b–e**, takes place in the course of this reaction. In order to investigate the process mechanism, a study was made of the kinetics of the hydrochlorination of the allenes **26e**,**f** in various solvents. The activation parameters, the isotope effect, and the influence of the solvent and nucleophilic additives agree with synchronous addition-elimination *via* a cyclic transition state involving the coordination of the acid proton to the ester oxygen and of the halogen to the central carbon atom of the allene system. It was shown that the two alternative mechanisms — the heterolytic mechanism (involving the protonation of the alkoxy-oxygen, the elimination of an alcohol molecule, and the subsequent attack by the nucleophile on the allyl carbonium ion) and the nucleophilic mechanism (*via* the attack of the halide anion on the central C atom of the allene system with subsequent elimination of an alcohol) — are unlikely. Thus the introduction of a new nucleophilic centre — the O atom of the ester group — into the allene promotes a change in the mechanism of the reaction with hydrogen halides.



26e,f **28b–e**

R = H (**26e**, **28b**,**d**); Me (**26f**, **28c**,**e**); X = Cl (**28b**,**c**), Br (**28d**,**e**).

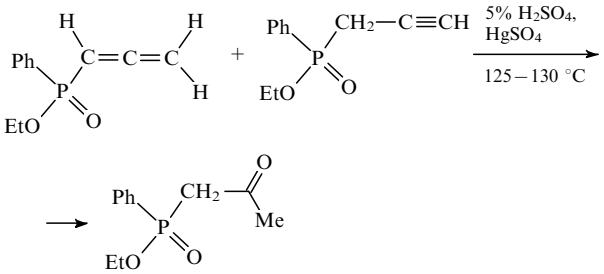
It has been suggested [120] that the allene–diene isomerisation of the chloroallenes **26g**,**h** proceeds similarly.



26g,h **28f,g**

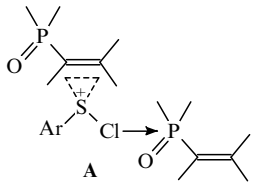
R = H (**26g**, **28f**); Me (**26h**, **28g**).

The hydration of the 1 : 1 mixture of the ethyl esters of phenylpropa-1,2-dienyl phosphinic and phenylprop-2-ynylphosphinlc acids in 5% H_2SO_4 in the presence of catalytic amounts of $HgSO_4$ afforded ethyl acetonyl(phenyl)phosphinate in 63% yield.[121] In the presence of H_2SO_4 and Hg^{2+} ions, water adds similarly to allenyldiphenylphosphine with formation of β-oxophosphine oxide.[12]



3. Reactions of phosphorylated allenes with sulfenyl chlorides

The interaction of sulfenyl chlorides and unsaturated phosphorus-containing compounds proved extremely interesting and made it possible to observe a series of non-trivial effects. For example, the study of the kinetics of this process demonstrated that it proceeds *via* an Ad_E3 mechanism and that two molecules of the unsaturated phosphorus-containing substrate participate in the formation of the transition state **A** of the rate-limiting stage of the reaction.[122]



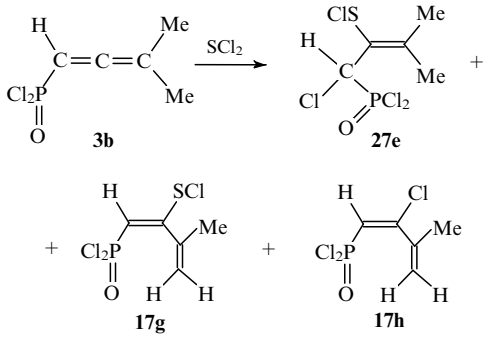
A

The study of the electrophilic sulfenylation of PA revealed also a series of features not characteristic of reactions of other electrophiles and determined, in the view of the majority of investigators, by the nature of the intermediate species.

The mode of interaction of sulfenyl chlorides with the dichlorides of alka-1,2-dienylphosphonic acids **3a**,**b** depends on the presence of substituents at the C(3) atom of the allene system.[123–128] If the C(3) atom is primary, the reaction leads to 2,3-adducts (with the ratio $E:Z = 85:15$ in the case of MeSCl or with 100% of the *E*-isomer for PhSCl).[124] If the C(3) atom is tertiary, then the products are the dichlorides of buta-1,3-dienylphosphonic acids.

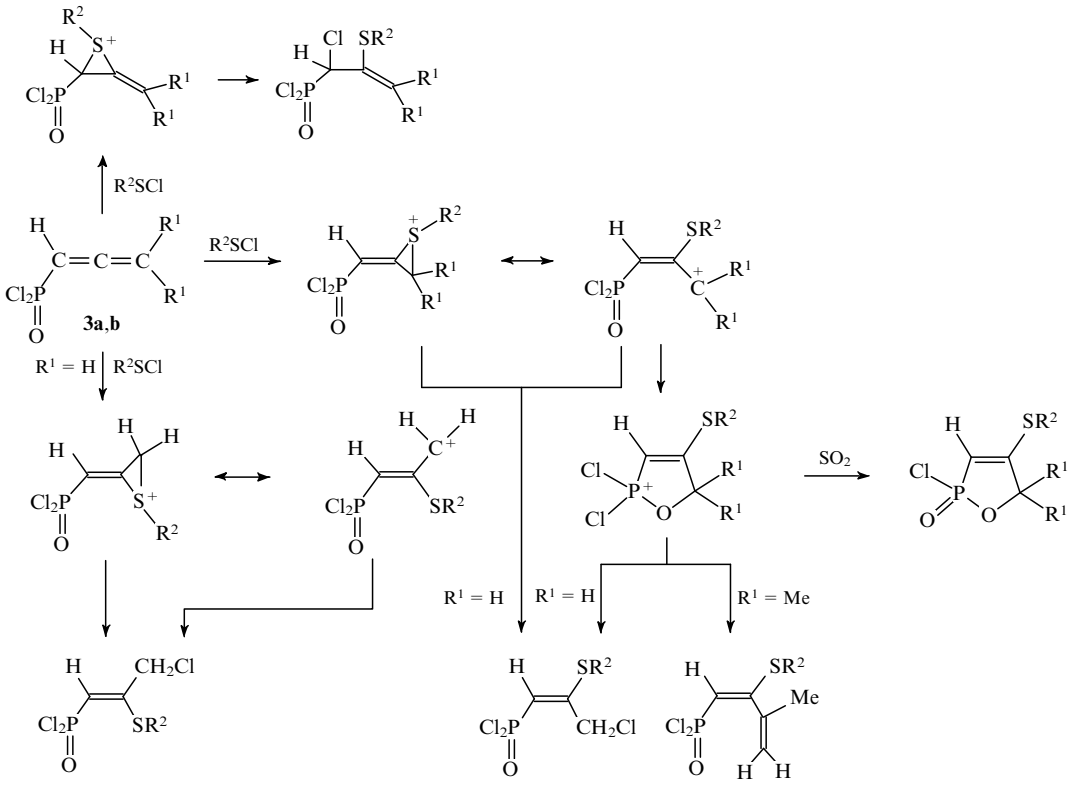
The reaction apparently proceeds *via* the formation of an episulfonium ion with its subsequent conversion into a tertiary carbonium ion (Scheme 11). According to a number of investigators,[1,124,125] the reaction proceeds as a rule *via* a cyclic phosphorane intermediate and the formation of different products is determined by the different directions of attack by the chloride ion. The yields of the products of these reactions (57%–63%) are lower compared with the halogenation reaction (85%–95%),[82–84] which suggests the occurrence of side reactions. Thus it has been shown [129] that the interaction of the dichlorides of 3,3-disubstituted allenylphosphonic acids **3a**,**b** and alkanesulfenyl chlorides affords the products of addition to the C(1) = C(2) bond apart from the 1,2-oxaphospholenes. The reaction is carried out in the presence of SO_2 as the fixator of the cyclic intermediate. The ratio of the 1,2-oxaphospholenes and the 1,2-adducts depends on the nature of the substituent at the S atom and on the reaction temperature. The change from R^1 = Me to R^1 = Bu^n and the lowering of temperature promote an increase in the yield of the 1,2-adducts.

The reaction of SCl_2 with the allene **3b** at room temperature leads to the formation of the adducts **27e** involving the C(1) = C(2) bond and the product **17g** resulting from the elimination HCl in proportions of ~5 : 3.[130,131] It is of interest to note that compound **17g** is the first representative of the previously unknown alkadienesulrenyl chlorides. Furthermore, the reaction mixture contains ~5% of the dichloride of 2-chloro-3-methylbuta-1,3-dienylphosphonic acid **17h**.



3b **27e** **17g** **17h**

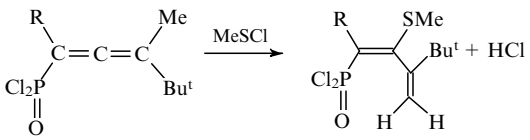
Scheme 11



It is believed [129] that the ratio of the 1,2-adduct and the cyclisation product reflect the stability of the episulfonium ions relative to carbonium ions. Effective cyclisation requires the formation of a free carbonium ion. In the episulfonium ion, the effective charge on the C(3) atom is reduced, which lowers the rate of cyclisation. Since the electronegative phosphoryl substituent destabilises the episulfonium ion to a lesser extent compared with the 'open-chain' α-carbonium ion, addition to the double bond adjoining the P atom also becomes possible.

In our view, the use in this instance of the concept of the 'episulfonium ion' is not altogether correct, because, firstly, episulfonium ions are fairly polar and sensitive to electronic factors [132] and, secondly, it had been shown earlier [132–134] that episulfonium ions are not in reality intermediates in Ad_E reactions of sulfenyl chlorides and the process proceeds *via* the formation of covalent sulfuranes or tight or solvent-separated ion pairs. It is logical to postulate that the intermediates in Ad_E reactions of sulfenyl chlorides with PA should be not sulfonium ions but much less polar structures. It is possible to account in this way for the formation of adducts involving the C(1)=C(2) bond in reactions with PA (although it is not clear why this process becomes dominant in certain cases).

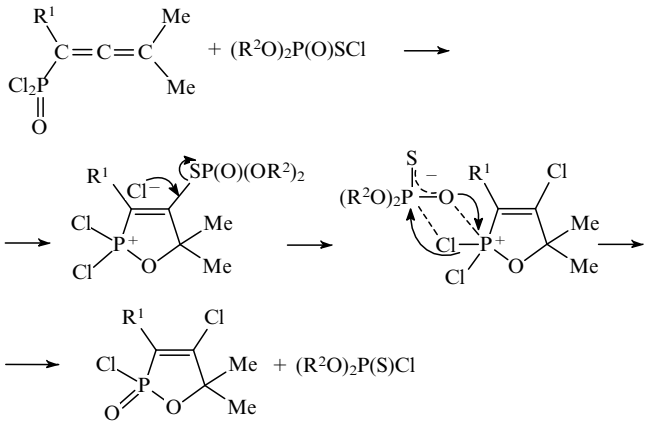
The reactions of the dichlorides of 1-substituted 3-(*tert*-butyl)alka-1,2-dienylphosphonic acid with MeSCl lead exclusively to 1,3-dienes.[75]



R = Ph, $MeOCH_2$.

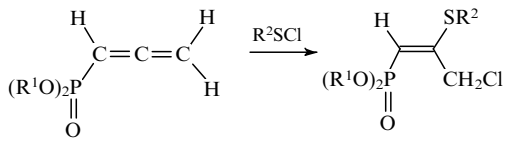
Dialkylphosphorylsulfenyl chlorides react with the dichlorides of alka-1,2-dienylphosphonic acids to form derivatives of 2,4-dichloro-2-oxo-1,2-oxaphospholene (Scheme 12).[124, 125] The interaction of alka-1,2-dienylphosphonic acid esters with sulfenyl chlorides is also determined by the structures of both the allene and the electrophile.

Scheme 12



The data on the reactions of propadienylphosphonic acid esters and R^2SCl (R^2 = Ph, Alk) are contradictory. The structure of the product of addition to the C(1)=C(2) bond in accordance with the Markovnikov rule was initially ascribed to the adduct.[135] However, subsequently the same workers [123–125] established the *E*-configuration of the adduct formed by addition to the C(2)=C(3) bond (Scheme 13). 2,4-Dinitrobenzenesulfenyl chloride does not react with PA.[127]

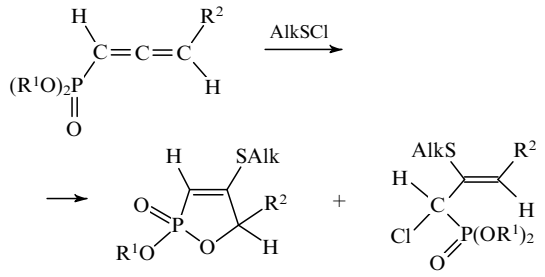
Scheme 13



R^1 = Alk; R^2 = Alk, Ph.

The interaction of alkanesulfenyl chlorides with propadienylphosphonates monosubstituted at the C(3) atom leads in all cases to a mixture of products of cyclisation and addition to the C(1)=C(2) bond (Scheme 14).[128]

Scheme 14

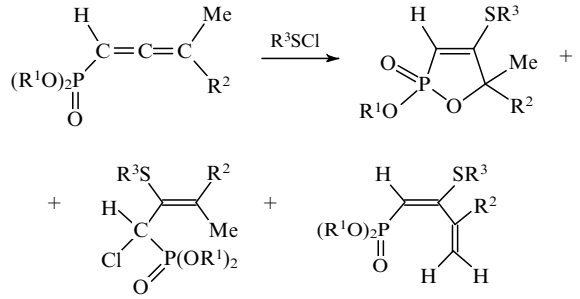


R^1 = Me, Et, Pr; R^2 = Me, Pr.

However, Khusainova *et al.*[126] obtained a mixture of the cyclisation products and the 1,2- and 2,3-adducts in proportions of 1 : 1 : 4 as a result of the reaction of buta-1,2-dienylphosphonic acid esters with MeSCl.

Apart from 1,2-oxaphospholenes, the products of the reactions of the dimethyl esters of 3-methylalka-1,2-dienylphosphonic acids with MeSCl are 1,2-adducts (8% – 15% for MeSCl) in the form of a mixture of the *E*- and *Z*-isomers in proportions ranging from 1.7 : 1.0 to 5 : 16.[136] Furthermore, the reaction of dimethyl 3-methylbuta-1,2-dienylphosphonate affords 4% – 7% of buta-1,3-dienylphosphonic acid esters (Scheme 15). The isolation of oxaphospholenes alone (63% – 82%) had been reported earlier.[137]

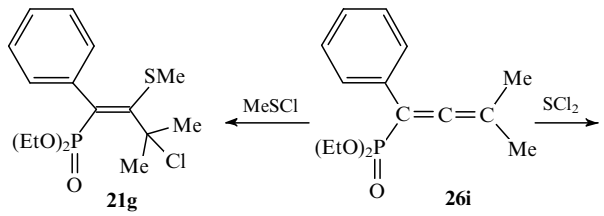
Scheme 15

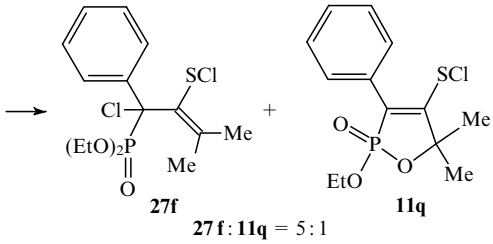


R^1, R^2 = Alk; R^3 = Cl, Me.

The analogous reaction with SCl_2 proceeds more selectively and leads to 4-chlorothio-1,2-oxaphospholenes in 92% – 95% yields.[138] The latter readily interact with nucleophiles, which makes it possible to introduce the oxaphospholene fragment into a wide range of organic substrates.[131, 139, 140] The study of the composition of the reaction mixture also made it possible to establish the formation of a 1,2-adduct (1% – 2%) and an alka-1,3-diene (4% – 7%).[131]

The principal product of the reaction of 3-methyl-1-phenylbuta-1,2-dienyl phosphonate **26i** with methanesulfenyl chloride is the adduct involving the C(2) = C(3) bond.[128] On the other hand, the interaction of compound **26i** with SCl_2 leads to the formation of predominantly the adduct **27f** involving the C(1) = C(2) bond, the structure of which has been confirmed unambiguously by ^{13}C NMR spectroscopic data.[131]

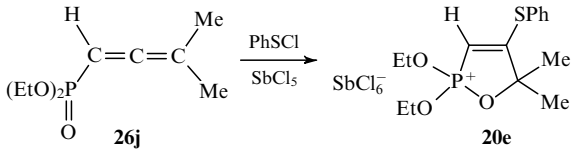




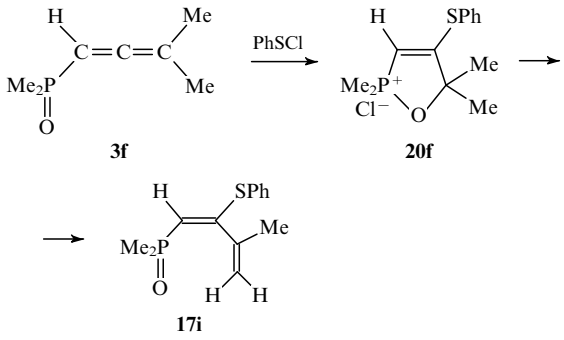
27f : **11q** = 5 : 1

On treatment with alkane(arene)sulfenyl chlorides, allenes containing a bridged substituent in the 3-position afford spiro-linked oxaphospholenes in 71% – 90% yield.[141] For PA incorporating the 1,3,2-dioxaphospholane ring, the ratio of oxaphospholenes and 1,2-adducts in reactions with alkane-sulfenyl chlorides is 4 : 1, the content of the 1,2-adducts falling to 5% on reducing the temperature from 20 °C to −60 °C.[142]

The stable quasi-phosphonium salt **20e** has been obtained by the interaction of the phosphonate **26j** with benzenesulfenyl chloride in the presence of $SbCl_5$.[143]



The reaction of benzenesulfenyl chloride with the PA **3f** leads to the quasi-phosphonium salt **20f** and, when the latter is heated *in vacuo*, HCl is split off and the corresponding 1,3-diene **17i** is formed.[124]



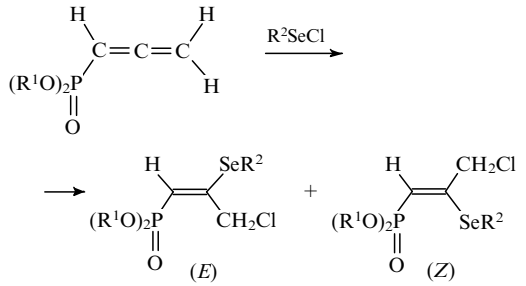
Thus many reactions of PA with sulfenyl chlorides proceed in a manner different from that of the reactions with other electrophiles and a situation which is at first sight paradoxical is observed: the fraction of the adducts involving the C(1) = C(2) bond increases with enhancement of the electron-accepting capacity of the substituent at this bond (transition from the dichlorides of allenylphosphonic acids to their esters). It has been postulated hitherto that the main cause of this difference is the possibility of the formation of cyclic intermediates. However, this is insufficient to account for the characteristic features of the reactions described in this section. As an example, we shall consider the interaction of PA and selenenyl chlorides — a class of electrophiles having properties close to those of sulfenyl chlorides, the addition of which to alkenes also proceeds *via* the formation of cyclic intermediates — episelenonium ions.

4. Reactions of phosphorylated allenes with selenenyl chlorides

The mode of the reactions of allenyl phosphonates with selenenyl chlorides also depends both on the structure of the electrophile and on the nature of the substituents at the C(3) atom of the allene system, but in all cases electrophilic attack is directed exclusively to the C(2) = C(3) bond. For example, on treatment with methane-

and benzene-selenenyl chlorides, the esters of propadienylphosphonic acid form 2,3-adducts; in the former case, the *E*- and *Z*-isomers are present in comparable amounts, while in the latter the *Z*-isomer predominates.[144] An interesting interpretation of the results of these reactions has been presented by Macomber *et al.*[127] On the basis of the allyl spin – spin coupling constant (1.5 Hz) and by analogy with the addition of sulfenyl chlorides, the *E*-configuration was attributed to the adduct of dimethyl propadienylphosphonate and benzeneselenenyl chloride (Scheme 16).

Scheme 16

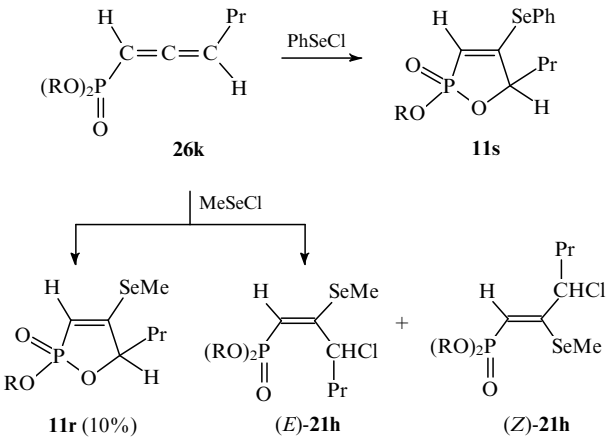


R^1 = Alk; R^2 = Me, Ph.

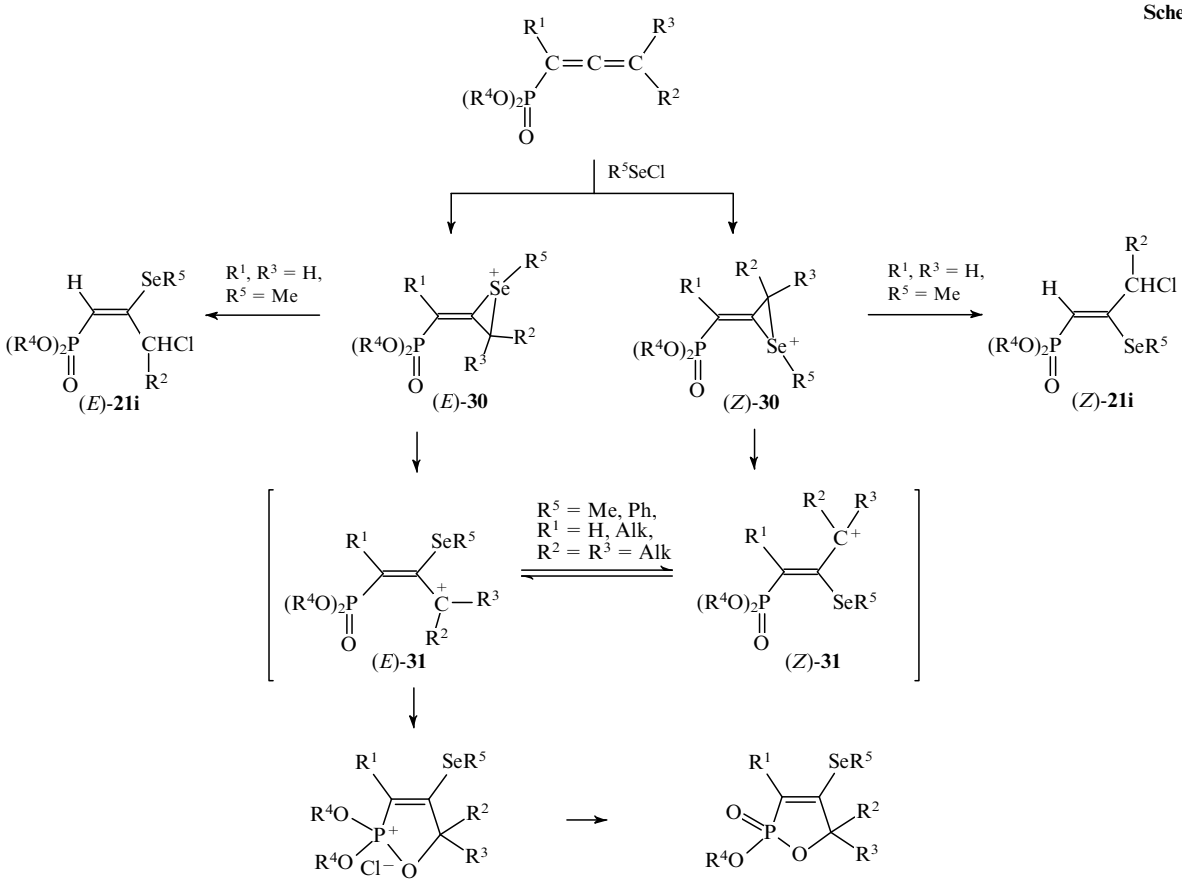
The interaction of the esters of 3-monosubstituted alkadienylphosphonic acids **26k** with methaneselenenyl chloride also results in the formation mainly of the adducts **21h** involving the C(2) = C(3) bond [the *E*- and *Z*-isomers are in proportions of 1 : 3], although the reaction mixture contains also ~10% of the oxaphospholene **11r**.[144] The analogous reaction with benzeneselenenyl chloride led to the isolation of only the oxaphospholene **11s** (Scheme 17).[127, 144]

The stereochemistry of the cyclisation of the allenylphosphonate **26l** has been investigated.[127] The reaction proceeds stereoselectively in acetonitrile [65% of (*E*)-**11t** and 35% of (*Z*)-**11t**], but selectivity is lost on passing to chloroform. This has been explained[127] by the different degrees of solvation of the intermediate phosphonium ion.

Scheme 17



Scheme 18



The interaction of esters of alka-1,2-dienylphosphinic and the corresponding phosphonic acids with methane- and benzeneselenenyl chlorides leads exclusively to phospholenes.[127, 144–146] Thus, in contrast to the reactions of PA with sulfenyl chlorides, in this case the addition to the C(1)=C(2) bond was not observed. The different stereoselectivity of the reactions of selenenyl chlorides has been explained [144] by the influence of the substituents at the Se atom and at the C(3) atom of the allene system on the relative stabilities of the intermediate selenonium and carbenium ions (Scheme 18). According to Angelov and Tancheva,[144] the oxaphospholenes are obtained from the (*E*)-**31** ion, while the 2,3-adducts are derived from the selenonium ions **30**, the preferential formation of the *Z*-isomers [141] being associated with the fact that the attack by the chloride ion on the selenonium ion (*Z*)-**30** proceeds more readily, for steric reasons, than the attack on the (*E*)-**30** ion.[141]

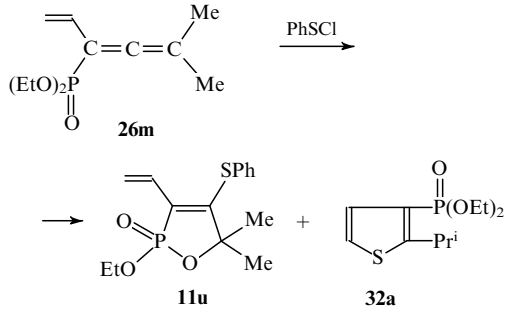
In our view, the mechanism of this reaction is more complex and, as in the case of sulfenyl chlorides, may involve the formation of tight and solvent-separated ion pairs.[132–134]

5. Reactions of hexa-1,3,4-trienyl and hexa-1,2,4-trienylphosphonic acids with sulfenyl and selenenyl chlorides

The introduction into the O=P–C=C=C system of additional nucleophilic centres, which can interact with electrophiles, increases significantly the reactivity of PA. The reactions of vinyl-substituted allenylphosphonates are extremely instructive in this respect.

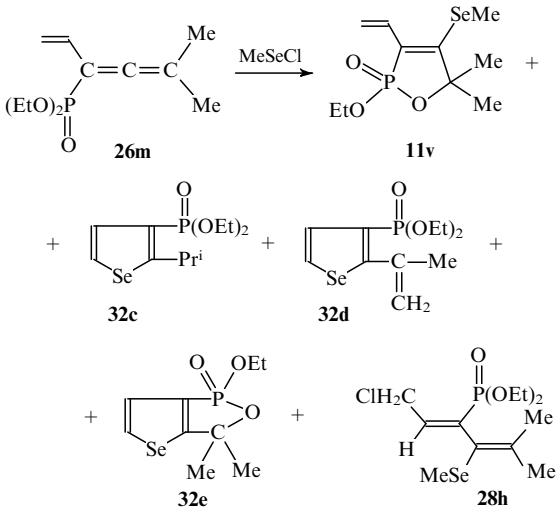
In the interactions with the halogens and sulfuryl chloride, these compounds exhibit the reactivity typical of allenyl phosphonates, forming derivatives of oxaphosphol-3-enes **11** or alka-1,3-dienylphosphonic acids **17** depending on the substituents at the P atom.[73, 74, 80, 88]

Diethyl hexa-1,3,4-trien-3-ylphosphonate **26m** reacts similarly with selenenyl chlorides,[80] but the reaction with sulfenyl chlorides proceeds *via* an unexpected path: together with the 1,2-oxaphospholene **11u**, the thiophene derivative **32a** is formed.[147] The product ratio varies as a function of the reaction temperature: **11u** : **32a** = 1.00 : 1.33 at 0 °C and 1.25 : 1.00 at −40 °C.

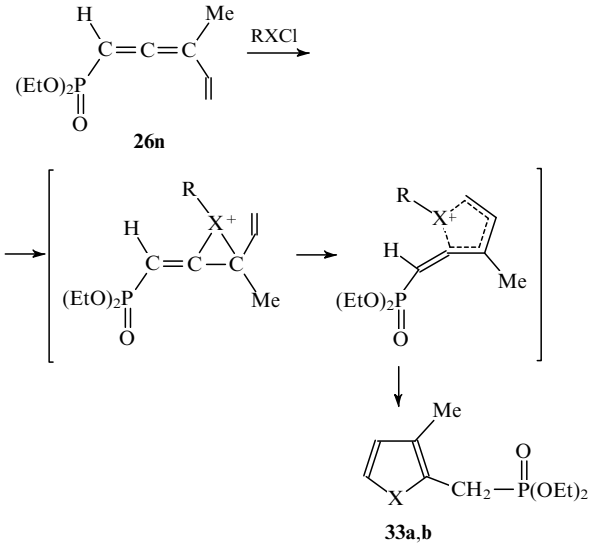


The formation of thiophenes is probably promoted by the same factors as the formation of the 1,2-adducts. This is confirmed, firstly, by the fact that the dichloride of hexa-1,3,4-trien-3-ylphosphonic acid affords exclusively the thiophene derivative **32b** in the analogous reaction [148] and, secondly, by the presence of only traces of similar products in reactions with selenenyl chlorides (see below), for which addition to the C(1)=C(2) bond is uncharacteristic.[144]

The interaction of the ester **26m** with selenenyl chlorides [149] leads to the formation of the 1,2-oxaphospholene **11u** as the main product. In addition, the heterocyclic compounds **32c–e** and the 1,4-adduct **28h** were obtained in an overall yield of 5%–12%.

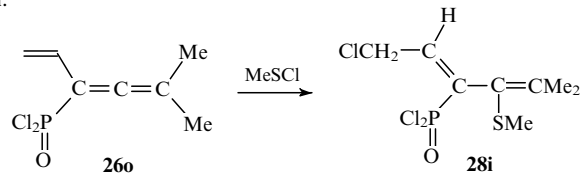


The reactions of diethyl penta-1,2,4-trienylphosphonate **26n** with alkanesulfenyl chlorides open a path to yet another class of substituted thiophenes — 2-thienylmethyl-phosphonic acids **33a**.[150] The interaction of compound **26n** with MeSeCl takes place similarly and leads to 2-selenophenylmethylphosphonic acid ester **33b**.[151]



X = S (**33a**), Se (**33b**); R = Alk.

The reaction of the dichloride of hexa-1,3,4-trien-3-ylphosphonic acid **26o** with MeSCl led to the formation of the 1,4-adduct **28i**.[148]

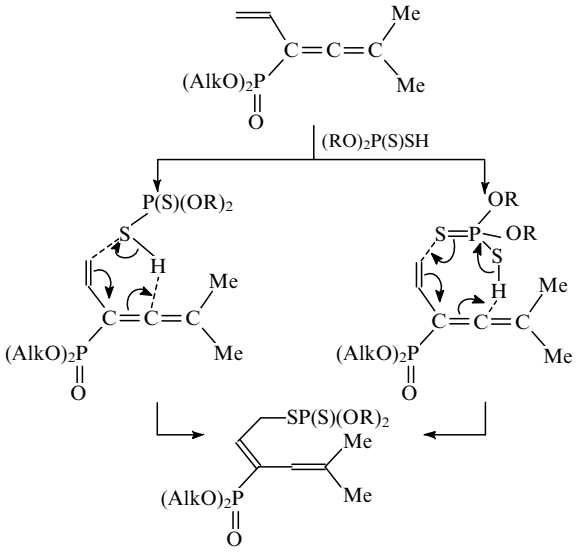


The formation of phosphorylated thiophenes (selenophenes) has been explained [145, 147–151] by the fact that the intermediate vinylepisulfonium (episelenonium) ions are capable of expansion to five-membered onium ions. The subsequent isomerisation and

dealkylation afford compounds **32a**–**c** and **33a**,**b**. The heterocyclic products **32d**,**e** are formed similarly.

The interaction of dialkyl hexa-1,3,4-trien-3-ylphosphonates with alkyldithiophosphoric acids has been described (Scheme 19).[117, 152] The reaction proceeds as addition to the 1,3-diene system. Two alternative mechanisms, involving either a six-centre or eight-centre transition state with participation of the thiol or thione sulfur, are apparently possible.

Scheme 19

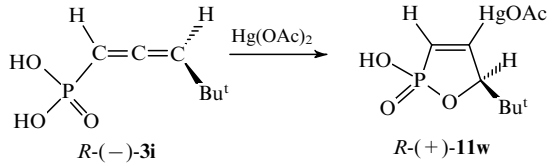


R = Alk.

Thus electrophilic attack on the C(1)=C(2) bond is also characteristic of the reactions of the dichlorides of vinyl-substituted PA with sulfenyl chlorides. The presence of functional groups gives rise to the possibility of additional reactions. Yet another direction in which the synthetic possibilities of PA may expand involves the use of new, less traditional electrophiles.

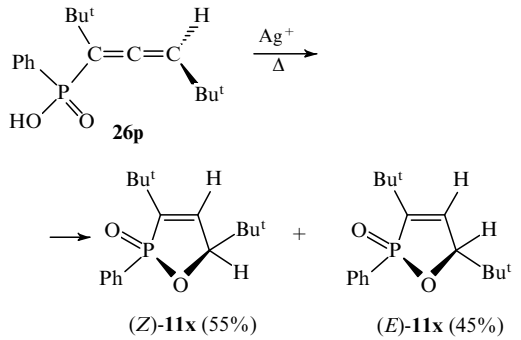
6. Reactions of phosphorylated allenes with other electrophiles

In the course of a study of the cyclisation of the optically active allenylphosphonic acid **3i** under the influence of mercury(II) acetate, it was shown [65] that it proceeds with 86% stereoselectivity (which is almost twice as high as the selectivity in the bromination reaction).



R-(−)-**3i** *R*-(+)-**11w**

The stereoselectivity of the cyclisation of the allenylphosphinic acid **26p** catalysed by Ag^+ ions has also been studied.[153]

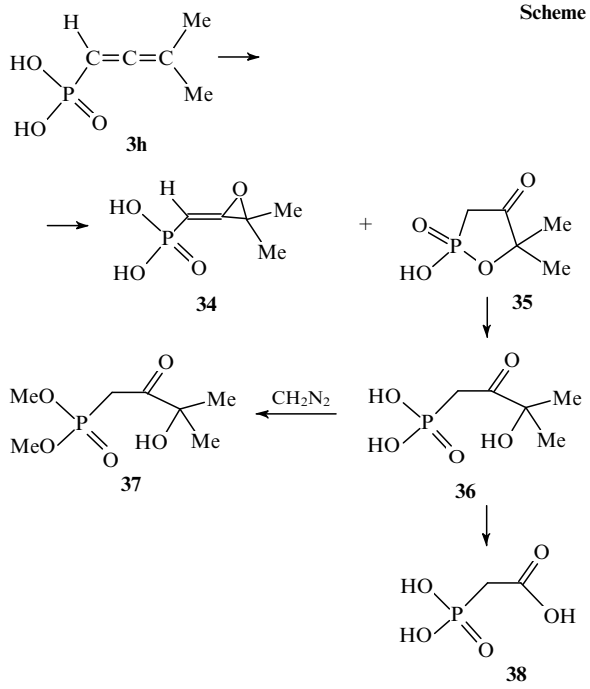


26p

(*Z*)-**11x** (55%) (*E*)-**11x** (45%)

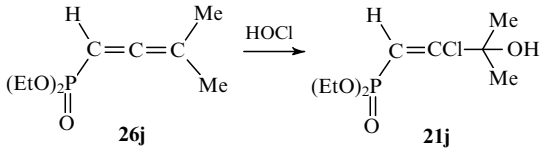
The reaction of the allenylphosphonic acid **3h** with percarboxylic acids has been investigated.[154] Compound **34**, formed initially, isomerises to the oxaphospholane **35**, which hydrolyses with ring opening and is converted into the oxophosphonate **36**. The latter may be converted into the dimethyl ester **37** by treatment with diazomethane or into the acid **38** by treatment with an excess of percarboxylic acid (Scheme 20).

Scheme 20



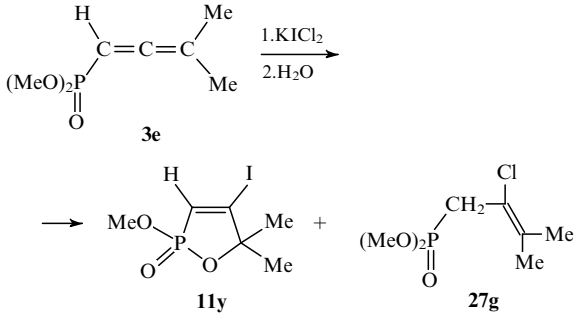
3h **34** **35** **37** **36** **38**

Hypochlorous acid reacts in an unusual manner with esters of 3,3-disubstituted alka-1,2-dienylphosphonic acids: 2,3-addition with formation of the phosphonate **21j** takes place instead of cyclisation.[155]



26j **21j**

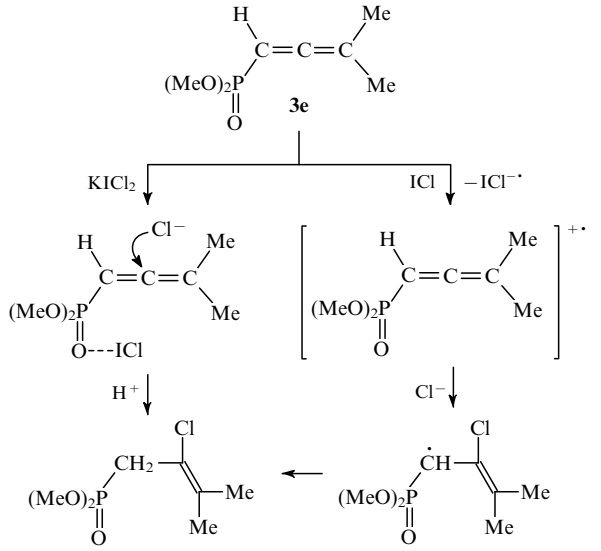
The presence in the molecules of PA of two double bonds with markedly different reactivities, one of which readily interacts with electrophiles whereas the other interacts with nucleophiles, made it possible to observe a new type of reactions of potassium dichloroiodate(I).[156] The formation of the main products of the interaction of the PA **3e** with $KICl_2$ corresponds to the formal addition of iodine chloride *via* the mechanism typical of reactions of electrophiles with the above substrates:



3e **11y** **27g**

The mechanism of the formation of compound **27g** has not been fully investigated. The regiospecificity of the addition of chlorine indicates that the acyclic phosphonate **27g** is formed as a result of nucleophilic attack by the chloride ion on the α,β-double bond with subsequent protonation of the intermediate. Here it is possible to put forward two versions of the reaction (Scheme 21).

Scheme 21

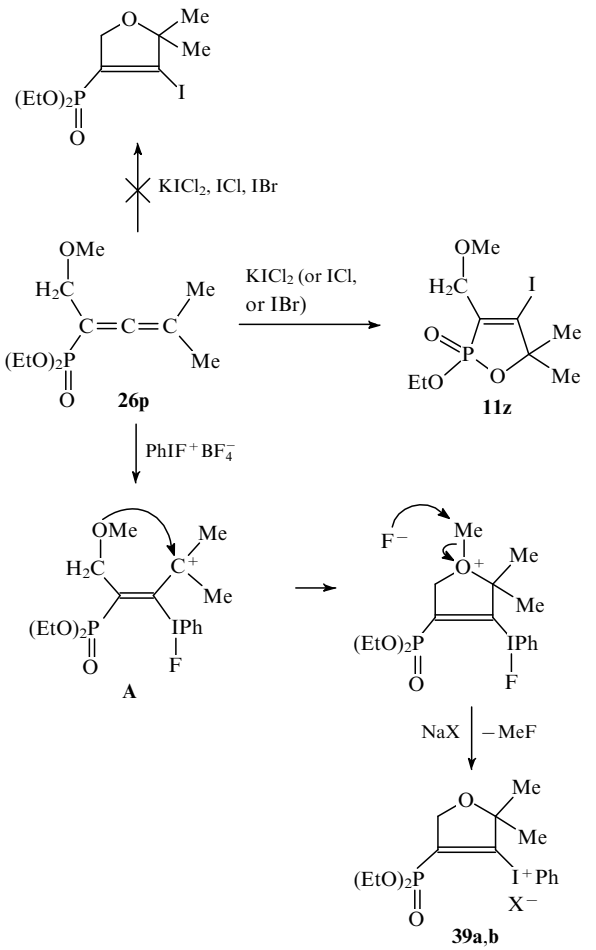


The first involves the nucleophilic addition of the chloride ion, promoted by the coordination of the intermediate iodine chloride, formed from the reagent, to the O atom of the phosphoryl group (ICl is known to exhibit the properties of a Lewis acid [157]). The alternative version is the SET mechanism which may occur in reactions of ICl with aromatic substrates.[158]

The methoxyallene **26p** reacts with $KICl_2$ [156] and interhalogens [72] with formation of 4-iodo-1,2-oxaphosphol-3-ene **11z**, while its interaction with a more polar iodine-containing reagent (the complex of difluoroiodobenzene with BF_3) leads to the dihydrofuran **39a** (yield 63%).[159] The same compound has been obtained by the reaction of the PA **29p** with iodosobenzene in the presence of an excess of BF_3 and subsequent treatment of the reaction mixture with a saturated aqueous solution of $NaBF_4$. When a $LiClO_4$ solution was used, the corresponding perchlorate **39b** was obtained in 48% yield. The addition of the electrophilic iodonium species to the allene **26p** proceeds regioselectively with formation of the stabilised allyl cation **A**. In the concluding stage, the methoxy-group functions as a nucleophile, which is accompanied by the formation of MeF and ring closure to give the furanyliodonium salt **39** (Scheme 22).

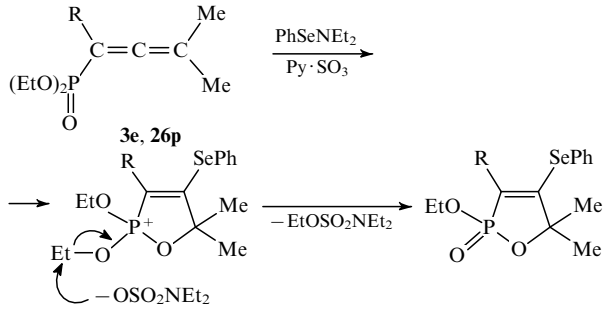
The reaction of *N*,*N*-diethylbenzeneselenenylamide with the allenylphosphonates **3e** and **26p** in the presence of an activator (a sulfonate), *i.e.* under conditions where weakly polar electrophilic species are generated,[160,161] proceeds with formation of 1,2-oxaphosphol-3-enes. As in the case of other weakly polar reagents, *anti*-attack by the electrophilic species relative to the phosphoryl residue is observed under these conditions. The subsequent cyclisation evidently takes place *via* the formation of a quasi-phosphonium salt containing the sulfamate ion as the

Scheme 22



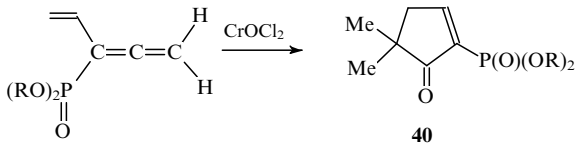
X = BF_4^- (**39a**), ClO_4^- (**39b**).

counterion. The nucleophilicity of the latter is sufficiently high for the rapid dealkylation of the quasi-phosphonium salt.



R = H, $MeOCH_2$.

The cyclopentenone derivative **40** can also be synthesised by the interaction of vinyl-substituted PA with chromyl chloride in anhydrous chloroform.[162] As in the reaction with iodonium salts,[159] *syn*-attack by the electrophile relative to the phosphoryl fragment occurs in this case.



40

R = Alk.

Thus the three examples presented indicate that the stereospecifity of the attack on functionally substituted PA by electrophiles and hence the type of cyclisation are correlated with the polarity of the attacking species. This is probably associated with the fact that more ionic, harder electrophiles are initially coordinated to the O atom of the phosphoryl group. This is indicated by data on the formation of complexes by allenylphosphine oxides with $NiCl_2$ [163] and also by the results of quantum-chemical calculations (see Section II).

IV. Conclusion

Analysis of the literature data shows that there is a possibility of electrophilic attack on all three reaction centres of the PA depending on the nature of the substituents in the allene system and at the P atom, the polarity of the electrophile, its capacity for preliminary coordination to the internal nucleophilic centres of the PA, and also the stability of the intermediate carbenium, phosphonium, and bridged onium ions. This is promoted by the asymmetry of the allene system, in which the HOMO is localised on the C(2) = C(3) bond, although the highest electron density is concentrated on the phosphorus-containing fragment and the C(1) = C(2) bond. Whereas positively charged species are coordinated primarily to the oxygen atom of the O = P group, uncharged electrophiles may attack either bond of the allene system. With certain exceptions, the electrophilic species then adds to the central carbon atom of the allene system, despite the fact that, according to the results of quantum-chemical calculations [49, 58] and ^{13}C NMR spectroscopic data,[59] the electron density on this atom is reduced compared with both terminal carbon atoms. On the other hand, quantum-chemical calculations confirm the presence of a considerable electron density on the C(2) atom for both the first and second occupied frontier orbitals of the allene [corresponding to a first approximation to the C(2) = C(3) and C(1) = C(2) bonds].

The molecular orbital perturbation theory may be used to explain and predict the chemoselectivity of the reactions of PA with electrophiles.[63] According to this theory, reactions with the early transition state may be controlled either by charge factors or by the interaction of the unoccupied MO of one reactant with the occupied MO of the other. The interaction of the frontier MO is of greatest importance; under these conditions, the greater the difference between the energies of the LUMO of the electrophile and the HOMO of the allene, the more probable is the attack on the C(1) = C(2) bond of the PA.

One of the factors influencing significantly the regiospecificity of the attack on the PA by the electrophile is steric hindrance. In the case of the weakest electrophile (the proton), the terminal carbon atom remote from the phosphorus atom is also attacked in reactions with certain monosubstituted PA and PA unsubstituted at the C(3) atom. The influence of steric factors also on the steriospecificity of the addition when the central atom is attacked is very appreciable. In the addition to the C(2) = C(3) bond, the reacting species usually attacks the PA from the side opposite to that of the phosphorus-containing fragment. The introduction of bulky substitutents in the 1-position in the allene system increases the amount of the *Z*-adduct involving the C(2) = C(3) bond. Another factor, which probably promotes the *syn*-addition of highly polar electrophiles, is their preliminary coordination to the hard nucleophilic centre comprising the oxygen atom of the O = P group. If other nucleophilic centres are present in the PA molecule, there is a possibility of the coordination of the electrophile to them also, which promotes the operation of additional reaction mechanisms.

Thus, by virtue of the high reactivity and the unusual properties of the system of closely linked unsaturated centres, characteristic of PA, the study of the reactions of these substrates with electrophiles constitutes an extremely interesting and timely problem. The investigation of the reactivities of new electrophiles in relation to PA makes it possible to expand the synthetic possibilities of these processes and to obtain various functionally substituted unsaturated organophosphorus compounds, which are promising from the standpoint of biological activity and their employment in fine organic synthesis. It also aids understanding of the nature of electrophilic processes.

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