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The Reactivity of Phosphorus-Containing Sulfenyl Chlorides in Addition Reactions

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THE REACTIVITY OF PHOSPHORUS-CONTAINING SULFENYL CHLORIDES IN ADDITION REACTIONS

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A systematic investigation of reactions of dialkoxyphosphoryl-(thiophosphoryl)sulfenyl chlorides with a wide range of unsaturated organic and elementoorganic compounds such as alkenes, alkynes, dienes, alkenylsilanes and -silatranes, alkenylstannanes, unsaturated phosphonates, unsaturated carboxylic acid derivaties, etc. has been performed. By means of a comparative analysis of the reactivity of phosphoryl- and organylsulfenyl chlorides in similar processes, the principal factors controlling the regiochemistry and the mechanism of the chlorothiophosphorylation of unsaturated systems as well as the character of unconventional Ad_E reactions have been identified.

Key words: Chloroorganylthiolphosphates, electrophilic addition, phosphorylsulfenyl chlorides

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1. INTRODUCTION

Phosphorus-containing sulfenyl chlorides (*P*-sulfenyl chlorides) are highly reactive electrophilic reagents capable of intensively interacting with various unsaturated compounds comprising both electron-donor and electron-withdrawing substituents. Chlorothiophosphorylation reactions allow various phosphorus-sulfur-containing compounds with a wide range of useful properties to be synthesized. Among the adducts of *P*-sulfenyl chlorides with unsaturated systems potent agricultural insecticides, lubricant additives, and antioxidants have been found. These electrophilic reagents possess a wide scope in preparative organic chemistry, providing for an easy functionalization of unsaturated compounds with simultaneous introduction into the molecule of a substrate, along with a bivalent sulfur atom, of chlorine and a phosphoryl group which, in turn, can be utilized for subsequent chemical transformations.

Unlike the chemistry of organylsulfenyl chlorides which has been studied in depth in a number of research centers,[1-9] the reactivity of the phosphorus-containing analogs is less well known. First Michalski's work dealing with the synthesis and reactions of *P*-sulfenyl chlorides was published as late as the mid-fifties.[10-11] Later this line of work was further developed by Polish authors,[12-13] Müller,[14] Almasi,[15] Gololobov,[16] Kutyrev,[17] and others. In these publications intriguing possibilities for the use of *P*-sulfenyl chlorides in organic synthesis have been demonstrated. It has also been found that their chemical behaviour in Ad_E reactions is characterized by a number of particular traits determined by the presence of a phosphoryl group in the electrophilic reagent, the electronic and steric effects of which have a noticeable influence not only on the rate and regiochemistry of addition but also facilitate unconventional interactions.

Reviews available in the literature[5-8,18,19] mainly deal with certain synthetic aspects of the chemistry of *P*-sulfenyl chlorides. In the present review for the first time an attempt has been made to pool and systematize data on the reactivity of phosphorus-containing sulfenyl chlorides in reactions with unsaturated organic and elementoorganic compounds, to perform a comparative analysis of the behavior of phosphoryl- and organyl-

sulfenyl chlorides in reactions and, finally, to unravel the factors (and first of all, the role of a phosphoryl group) contributing to the mechanisms of these processes.

2. SYNTHESIS OF *P*-SULFENYL CHLORIDES

2.1. Phosphorylsulfenyl Chlorides

One of the widely used methods of obtaining dialkoxyphosphorylsulfenyl chlorides is the reaction of trialkyl thiophosphates with thionyl chloride or with chlorine.[20-24]

$$(RO)_3P{=}S + SO_2Cl_2 \xrightarrow{-10\,^\circ C} (RO)_2P(O)SCl + RCl + SO_2$$

$$(RO)_3P{=}S + Cl_2 \xrightarrow{-10\,^\circ C} (RO)_2P(O)SCl + RCl$$

R = Me, Et, Pr, *i*-Pr, Bu, Me_3Si; R_2 = $(CH_2)_2CH(CH_3)$, $CH_2C(CH_3)_2CH_2$

This reaction (the Michalski reaction) proceeds under mild conditions and is characterized by high yields.

When *O,O*-dialkyl *O*-trimethylsilyl thiophosphates are employed, the interaction with sulfuryl chloride results in the quantitative formation of *P*-sulfenyl chlorides which require no further purification.[25]

$$(RO)_2P(S)OSiMe_3 + SO_2Cl_2 \xrightarrow[-SO_2]{-20\,^\circ C} (RO)_2P(O)SCl + Me_3SiCl$$

Dialkoxyphosphorylsulfenyl chlorides can be synthesized from dialkylthiophosphoric acids or their salts.[10,11]

$$(RO)_2P(S)OR^1 \xrightarrow{SO_2Cl_2} (RO)_2P(O)SCl + R^1Cl + SO_2$$

R = alkyl; R^1 = H, K, Na

It has been found that bis(dialkoxyphosphoryl) disulfides are formed as intermediates which are subsequently cleaved by sulfuryl chloride at the S–S bond and form two molecules of the *P*-sulfenyl chloride.[11]

The final stage of this process is the basis for a specific method of phosphorylsulfenyl chloride production.[26,27] Bis(dialkoxyphosphoryl) disulfides can be easily synthesized by reaction of dialkylphosphorous acids with sulfur chlorides:

$$2\ (RO)_2P(O)H \xrightarrow{S_2Cl_2} (RO)_2P(O)S\text{–}S(O)P(OR)_2 \xrightarrow[-SO_2]{SO_2Cl_2} 2\ (RO)_2P(O)SCl$$

Alkoxyalkylphosphorylsulfenyl chlorides are obtained upon interaction of sulfuryl chloride with dialkoxyalkylthionophosphates[28] or *O*-alkylalkylthiophosphonic acids.[29]

$$R(R^1O)\overset{S}{\overset{\|}{P}}OR^2 \xrightarrow{SO_2Cl_2} R(R^1O)\overset{O}{\overset{\|}{P}}SCl + R^2Cl + SO_2$$

R = Et, *t*-Bu; R^1 = Et, Bu; R^2 = H, alkyl

However, *P*-sulfenyl chlorides containing a P–C bond are far less stable than dialkoxyphosphorylsulfenyl chlorides. They decompose readily and form chlorophosphonates.

$$R(R^1O)P(O)SCl \longrightarrow R(R^1O)P(O)Cl + S$$

Only with the employment of *t*-butylthionophosphonic ester *t*-butylalkoxyphosphorylsulfenyl chloride has been obtained in quantitative yield.[28]

Alkoxyalkylphosphorylsulfenyl chlorides can also be formed upon the interaction of *O*-alkyl-alkylchlorothionophosphonates with sulfuryl chloride.[30]

$$R(R^1O)P(S)Cl \xrightarrow{SO_2Cl_2} R(R^1O)P(O)SCl + SOCl_2$$

If the initial compound is an *O,O*-dialkylchlorothionophosphonate, the process proceeds according to the chlorodealkylation scheme, resulting in the formation of an alkoxychlorophosphorylsulfenyl chloride.[31,32]

$$(RO)_2P(S)Cl + SO_2Cl_2 \longrightarrow Cl(RO)P(O)SCl + RCl + SO_2$$

2.2. *Thiophosphorylsulfenyl Chlorides*

Dialkoxythiophosphorylsulfenyl chlorides are usually obtained by reaction of dialkoxythiophosphorylsulfenamides with hydrogen chloride.[33–36]

$$(RO)_2P(S)SNR^1{}_2 \xrightarrow{HCl} (RO)_2P(S)SCl + R^1{}_2NH\cdot HCl$$

R = alkyl; R^1 = $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$

Phosphorus dithioacids as well as bis(dialkoxythiophosphoryl) disulfides do not produce thiophosphorylsulfenyl chlorides with chlorine or sulfuryl chloride: the process acquires a more complicated character with the participation of the P=S group.[37,38]

Similar to phosphorylsulfenyl chlorides, the stability of thiophosphorylsulfenyl chlorides sharply decreases when alkoxy groups at the phosphorus atom are replaced by alkyl or aryl groups.[35,36,39] Individual dialkyl(aryl)thiophosphorylsulfenyl chlorides are not obtainable.[35]

There are also several special methods of thiophosphorylsulfenyl chloride synthesis. For example, a reaction of *S*-di(neopentoxy)thiophosphoryl-*O*-neopentylsulfenate and

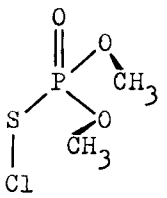
trimethylchlorosilane has been described, the result of which is di(neopentoxy)thiophosphorylsulfenyl chloride.[40]

$$(Me_3CCH_2O)_2P(S)SOCH_2CMe_3 + Me_3SiCl \longrightarrow (Me_3CCH_2O)_2P(S)SCl + Me_3SiOCH_2CMe_3$$

3. CONFORMATION OF *P*-SULFENYL CHLORIDES

According to combination scattering spectroscopy data a dimethoxyphosphorylsulfenyl chloride molecule possesses two preferential conformations, the energy difference of which is 3.8 kJ/mole.[17] Since changes in the temperature and polarity of the medium are accompanied by changes of the band intensities of the P–O–C deformation vibrations and the full-symmetrical oscillations ν (PO_2) and provided that the spectral features due to the P–S–Cl group remain unchanged it can be concluded that the cause of the conformational isomerism of the *P*-sulfenyl chloride is rotation around the P–O bond rather than the P–S bond.

On the basis of dipole moment data the type of rotational isomers formed has been established.[17] The comparison of the experimental dipole moment for dimethoxyphosphorylsulfenyl chloride with those calculated for possible conformations where the methyl groups and a S–Cl bond are *gauche*-, *trans*-, or *cis*-positioned with respect to P=O indicates the existence of two forms with *trans*-orientation of the S–Cl and P=O bonds. Here, the methyl groups are *gauche*-positioned, like in other phosphates and phosphonates.[41,42]



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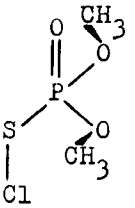

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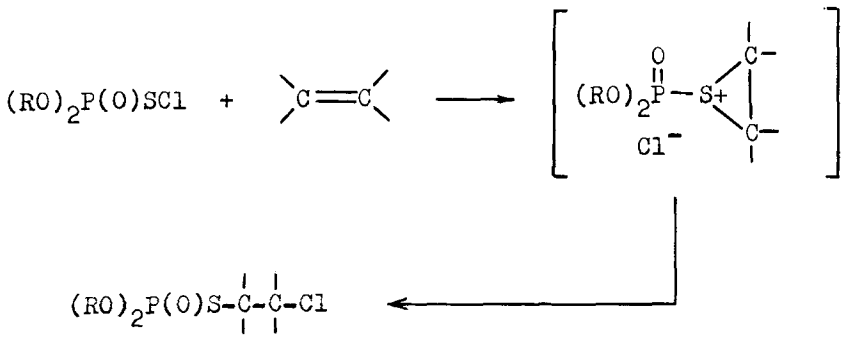
4. REACTIONS WITH OLEFINS

4.1. With Alkenes

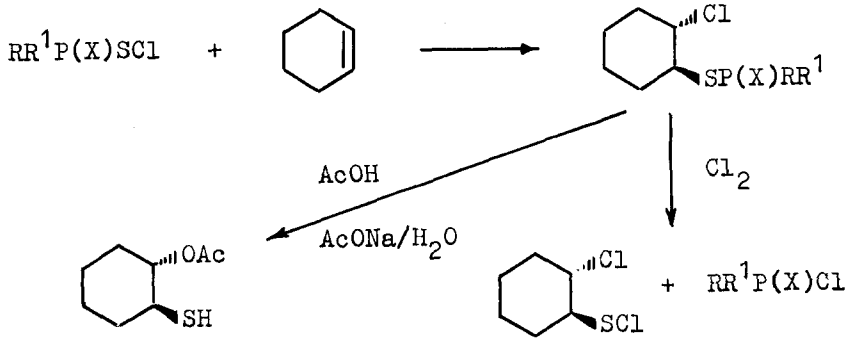
Michalski and coworkers have established that phosphorylsulfenyl chlorides containing an electrophilic sulfur atom in a P–S–Cl fragment, like organylsulfenyl chlorides,[1-8] are capable of ready addition to alkenes with the formation of *S*-2-chloroalkylthiophosphates.[10-13,29,43-47]



By analogy with the well-known Ad_E mechanism of organylsulfenyl chloride reactions,[1-3,8,9] the formation of an episulfonium intermediate which is opened by attack of the chloride anion has also been assumed in this process.[45,48]

Dialkoxyphosphorylsulfenyl chlorides interact both with symmetric (i.e. ethylene,[17,27,43,44] stilbene,[12] tetramethylethylene,[12] cyclohexene[12,48]) and asymmetric olefins.[5-8,14,43,49]

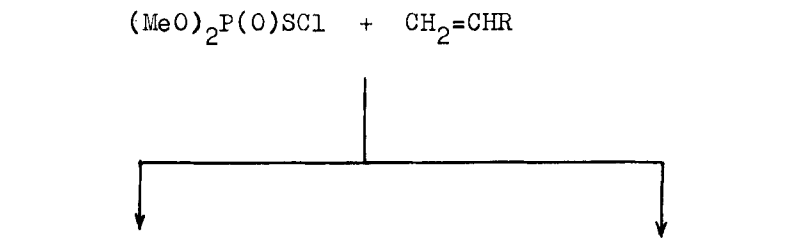
By means of ^1H, ^{13}C, and ^{31}P NMR spectroscopy the exceptional formation of *trans*-adducts[15,48,50,51] has been established in the reactions of *P*-sulfenyl chlorides with cyclohexene. These adducts can either be dephosphorylated by chlorine[48] or by acetic acid.[50]



R,R^1 = AlkO; R = Alk; R^1 = AlkO; R = *t*-Bu; R^1 = Ph; X = O, S

Interaction with asymmetric alkenes, as a rule, leads to mixtures of isomeric adducts the proportions of which do not substantially depend on the experimental conditions (i.e. reaction temperature, the nature of the solvent, the presence of acidic impurities) but are determined by the electronic and steric effects of the substituents in the olefin.[14]

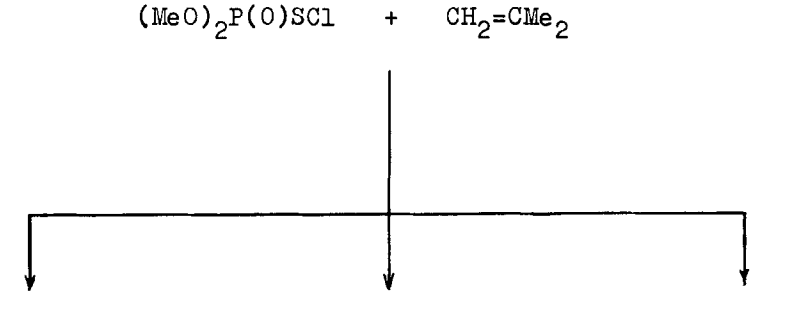
Thus, it has been shown[14,49] that with an increase in the volume of the substituent R at the double bond (a transition from propene to 1-pentene), the contents of regioisomer **2** increases, and this phenomenon is associated with the steric control of the nucleophilic attack by chloride anion of a cyclic intermediate. If the electronic nature of the substituent R permits it to participate in the stabilization of a partial positive charge at a neighbouring carbon atom of the intermediate (R = $CH{=}CH_2$) the most preferred pathway is that leading to isomer **1**.



$(MeO)_2P(O)SCH_2\underset{Cl}{\underset{|}{C}}HR$ (1) $(MeO)_2P(O)S\underset{R}{\underset{|}{C}}HCH_2Cl$ (2)

R	1 : 2 (%)
CH_3	49 : 51
C_3H_7	35 : 65
$CH_2=CH$	73 : 27

At the same time, an important part in the direction of the interaction of *P*-sulfenyl chlorides with alkenes is played by the phosphoryl group, the electron-withdrawing effect of which determines the formation of considerable positive charge at the carbon atoms of an unsaturated center in the course of the Ad_E reaction. As a result deprotonation of the intermediate may take place. This is evident in the reaction of dimethoxyphosphorylsulfenyl chloride with isobutene where, along with the adducts **3** and **4** *O*,*O*-dimethyl-*S*-2-methylpropenylthiophosphate **5** is obtained.[14,49]



$(MeO)_2\overset{O}{\overset{\|}{P}}SCH_2CMe_2Cl$ (3, 57 %) $(MeO)_2\overset{O}{\overset{\|}{P}}SCMe_2CH_2Cl$ (4, 19 %) $(MeO)_2\overset{O}{\overset{\|}{P}}SCH_2\overset{Me}{\overset{|}{C}}=CH_2$ (5, 21 %)

A comparative analysis of the reaction paths of methyl-,[49] dimethylamino-,[52] aryl-[49,53] acetylthio-,[54] and phosphorylsulfenyl chlorides[49] with propene and isobutene shows that

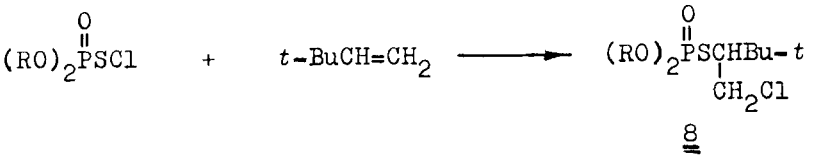
with increasing electron-withdrawing effect of the substituent at the sulfur atom of the sulfenyl chloride the yield of the adduct **6** increases according to Markovnikov's rule.

R	**6**:**7** (R^1 = Me; R^2 = H) (%)	**6**:**7** (R^1 = R^2 = Me) (%)
CH_3	18:82	20:80
$(CH_3)_2N$	22:78	29:71
C_6H_5	32:68	–
4-ClC_6H_4	38:62	12:88
$CH_3C(O)S$	40:60	68:32
$(CH_3O)_2P(O)$	49:51	57:19*

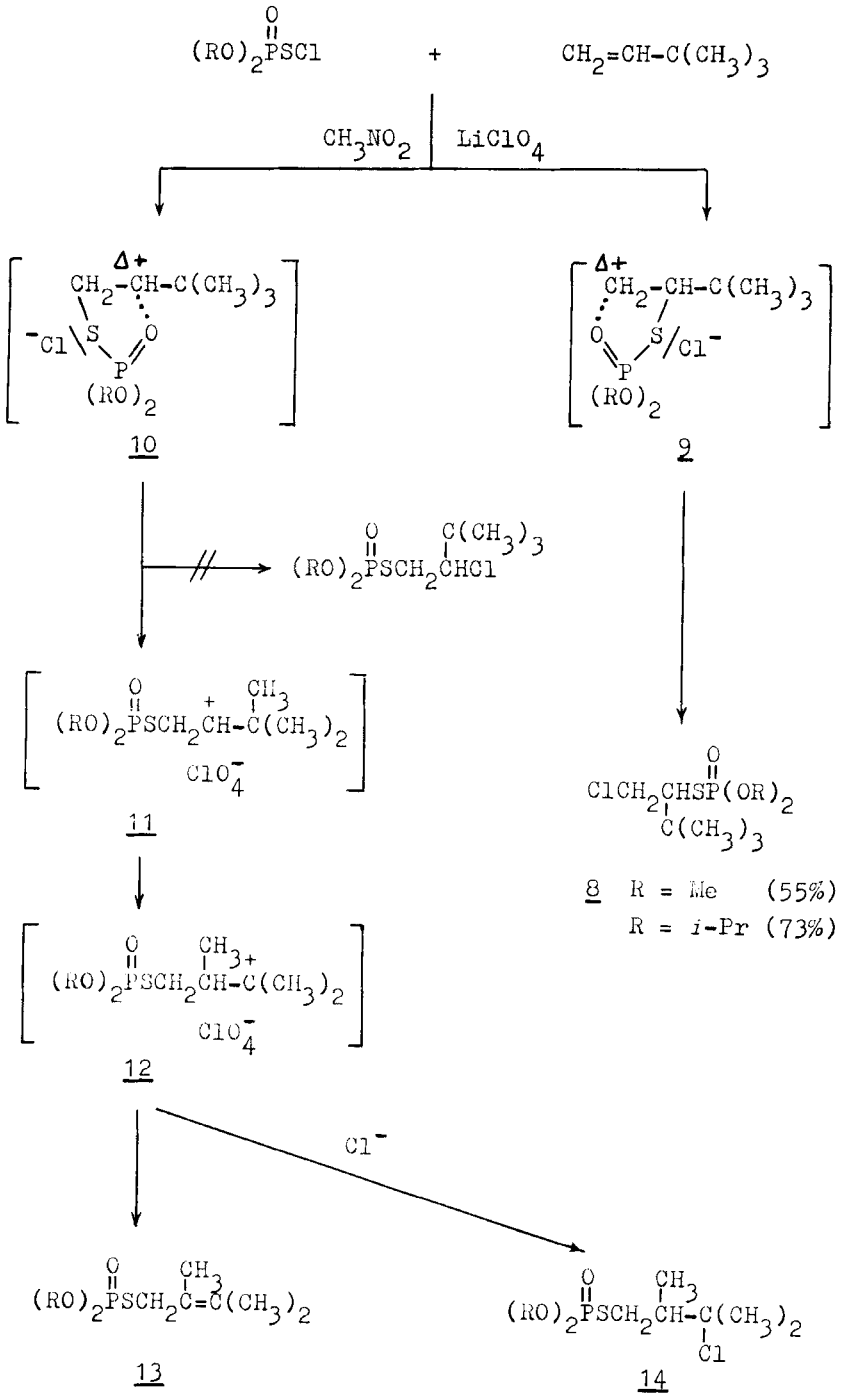
*Thiophosphate **5** (21%) was also obtained.

Obviously, this is the result of a reduced n-donor function of the sulfur atom and a decrease in the efficiency of the reverse ($n \rightarrow \pi^*$) electron density transfer to the reaction center which increases the participation of an alkyl substituent at the double bond in the stabilization of a partial positive charge of the intermediate. This factor acquires special significance in the case of *P*-sulfenyl chlorides where an electron-withdrawing phosphoryl group is directly linked to the sulfur atom.

With the introduction of a bulky *t*-butyl group into the alkene the steric accessibility of the neighboring sp^2-carbon atom is sharply reduced. Therefore, the addition of *P*-sulfenyl chlorides proceeds in a regioselective manner.[55]



However, when the reaction is performed in a nitromethane-lithium perchlorate system where effective solvation of ionic structures is possible,[56] along with the formation of the adduct **8**, σ-rearrangements take place which result in formation of the thiophosphates **13** and **14**.[55] We assume that this interaction involves the formation of the carbenium type intermediates **9** and **10** which are distinguished by the relative orientation of the reagents (Scheme 1). It should be noted that the S–Cl bond of the phosphorylsulfenyl chloride, unlike organic analogs,[56] has been preserved in the CH_3NO_2-$LiClO_4$ system, according to combination scattering spectroscopy data. Evidently the stabilization of the partial positive charges in the intermediates **9** and **10** is mainly provided by the phosphoryl oxygen and not the sulfur atom of the *P*-sulfenyl chloride. This is indicated both by low nucleophilicity of the sulfur atom in thiolophosphates (they are not subject to *S*-alkylation[57] and by the dependence of the regiochemistry of the addition on the bulk of the substituents at the phosphorus atom). Bonding of the sulfur atom to the α-carbon of an unsaturated center results in adduct

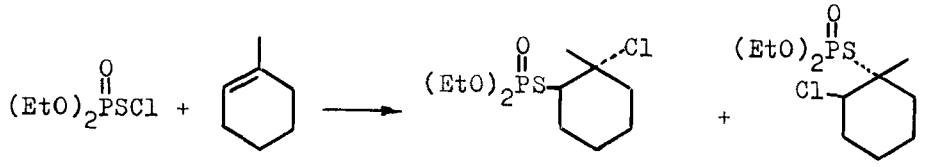


Scheme 1.

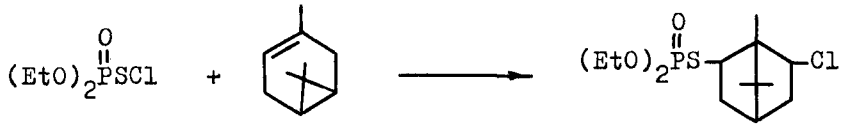
8. The formation of intermediate **10** is sterically hindered; therefore, this Ad_E process is disfavored in a medium of low polarity. In the nitromethane-lithium perchlorate system the intermediate **10** can be transformed into the tertiary carbocation **11** and this provides for the possibility of a 1,2-shift of the methyl group from the *t*-butyl group to the neighboring carbon atom. Subsequent deprotonation of intermediate **12** leads to the unsaturated thiolophosphate **13**. Adduct **14** may be the result of the attack of chloride on the carbenium center of intermediate **12** or of the addition to thiolophosphate **13** of hydrogen chloride present in the reaction mixture.[55]

The fact that the yield of adduct **8** increases when the methoxy group at the phosphorus atom is replaced by the more bulky isopropoxy group proves the participation of the phosphoryl group of the sulfenyl chloride in the stabilization of the carbenium centers of intermediates **9** and **10**. Here, more advantageous steric conditions are attained in the structure **9** and therefore, in case of diisopropoxyphosphorylsulfenyl chloride, the reaction leads mainly to the formation of thiolophosphate **8**.

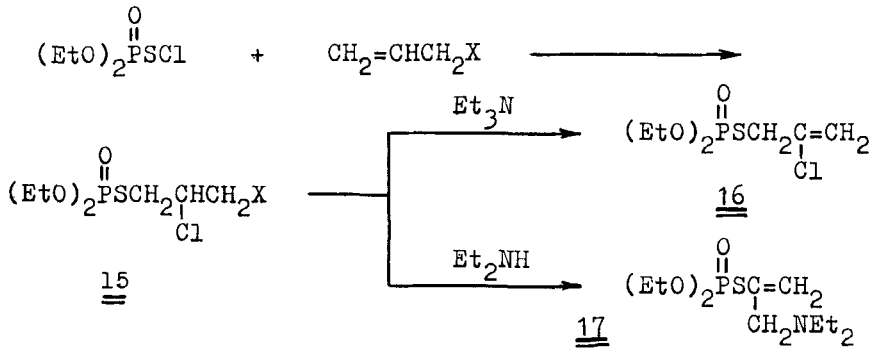
Phosphorylsulfenyl chlorides can be easily added to substituted cycloolefins and form a mixture of regioisomers.[58]



In the case of α-pinene the Ad_E process is accompanied by a Wagner-Meerwein rearrangement.[59]



It has been established that diethoxyphosphorylsulfenyl chloride adds regioselectively to allyl halides.[60] When adduct **15** is treated with a tertiary amine *S*-2-chloroallylthiophosphate **16** is obtained. If a secondary amine is used substitution of a halogen atom by an amino group takes place as well as 1,2-migration of the thiophosphate group with subsequent elimination of hydrogen halide and formation of *O,O*-diethyl-*S*-(1-diethylaminomethyl)vinylthiophosphate **17**.[60]



4.2. *With Arylethylenes*

4.2.1. Regiochemistry The regiochemistry of *P*-sulfenyl chloride addition to arylethylenes is determined not only by the electronic effect of an aromatic substituent in the unsaturated compound, but also by the steric effect of the alkoxy groups at the phosphorus atom.[14,17,45,61] An electron-donor effect of an aromatic group promotes β-orientation of the thiophosphoryl group. This factor plays a decisive role in reactions with dimethoxyphosphorylsulfenyl chloride: *O,O*-dimethyl-*S*-2-aryl-2-chloroethylthiophosphates are mainly formed.[14,17,61]

$$(MeO)_2\overset{O}{\overset{\|}{P}}SCl + p\text{-}XC_6H_4CH{=}CH_2 \longrightarrow p\text{-}XC_6H_4\underset{Cl}{\underset{|}{C}}HCH_2S\overset{O}{\overset{\|}{P}}(OMe)_2$$

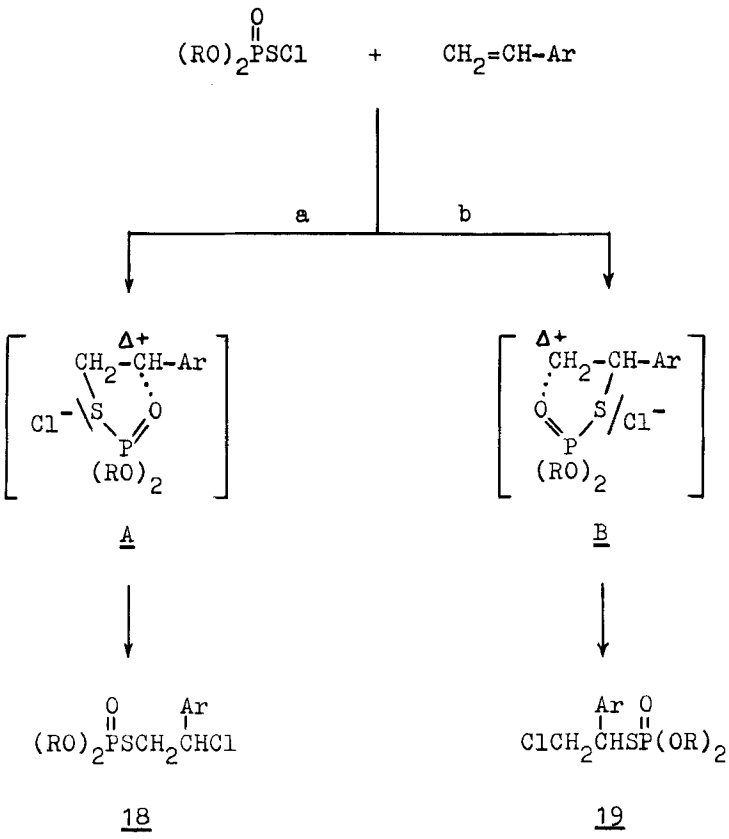
X = MeO, Me, $ClCH_2$, F, Cl, Br, NO_2

However, with the increasing volume of the alkoxy groups at the phosphorus atom (*i*-PrO), the importance of the steric effect is also increasing and this leads to a loss of regioselectivity and the formation of a mixture of the isomeric adducts **18** and **19**.[61] The ratio **18**:**19** depends neither on the reaction temperature nor on the presence of acidic impurities. The yield of β-chloroorganylthiophosphate **19** increases with decreasing electron donor properties of the aryl substituent. A similar dependence of the regiochemistry on the steric features of the electrophile is indicative of the formation of the cyclic intermediates **A** and **B** in which the phosphoryl group of the *P*-sulfenyl chloride participates in the stabilization of a partial positive charge (Scheme 2).

If the size of the RO group is small the electron-donor effect of the aromatic substituent plays a decisive role, forcing the process to take pathway (a), although the steric orientation of the phosphoryl group in the intermediate **A** is unfavorable, both with regard to the position of the aryl and alkoxy groups and the steric hindrance of the chloride attack.

With increasing bulk of the alkoxy substituents in the electrophile the steric factor acquires even greater significance, and this leads to a partial change in the orientation of the reagents and the formation of a mixture of the regioisomers **18** and **19**. However, an increasing donor effect of the aromatic group (*p*-methoxystyrene) provides for the possibility of effective stabilization of a positive charge at the α-carbon atom without active participation of the P=O group. The reaction proceeds regioselectively irrespective of the steric accessibility of the phosphorus group.

4.2.2. Kinetics and mechanism The addition of *P*-sulfenyl chlorides to arylethylenes, irrespective of its regiochemistry, takes place within the framework of the common Ad_E2 mechanism.[61,62] This is proven by the correlation of the second-order rate constant logarithms of the reactions of dimethoxy- (k_1) and diisopropoxyphosphorylsulfenyl



Ar	18 : 19 (R = *i*-Pr)
4-$MeOC_6H_4$	100 : 1
4-MeC_6H_4	80 : 20
C_6H_5	65 : 35
4-FC_6H_4	60 : 40
4-ClC_6H_4	50 : 50
4-BrC_6H_4	50 : 50
4-$NO_2C_6H_4$	50 : 50

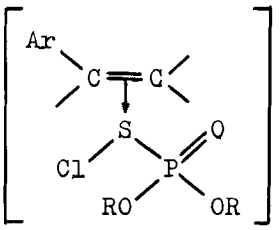
Scheme 2.

chloride (k_2) with arylethylenes (dichloroethane, 25 °C) with the substituent electrophilic constants of the aromatic ring of the unsaturated reagent.

$$\lg k_1 = -(1.42 \pm 0.01) - (3.17 \pm 0.37)\,\sigma^+$$
$$R = 0.990;\ S_0 = 0.115;\ n = 6$$
$$\lg k_2 = -(1.37 \pm 0.02) - (2.37 \pm 0.07)\,\sigma^+$$
$$R = 0.999;\ S_0 = 0.043;\ n = 6$$

The rate of the interaction sharply decreases with the introduction of donor groups at the phosphorus atom: the rate constant of the reaction of methylmethoxyphosphoryl-sulfenyl chloride with styrene is 1/270 of that of dimethoxyphosphorylsulfenyl chloride.[62] Thus, the electron density at the sulfur atom is much higher in the activated complex, compared to the initial electrophile.

Kinetic data set allowed us to assume that at the initial stage of the interaction of *P*-sulfenyl chlorides with arylethylenes the shift of electron density from the π-system of the unsaturated reagent towards the σ^*-orbital of the S–Cl bond ($\pi \rightarrow \sigma^*$ transfer) is dominating.[63–65] It is favored by donor substituents in the styrene and by acceptor substituents in the phosphorus reagent.[61,62] The transition state of the Ad_E reaction's limiting stage has the structure of a π-complex **20**.[65] In reactions with organylsulfenyl chlorides this process ($\pi \rightarrow \sigma^*$ transfer) is accompanied by an inverse electron transfer from the sulfur atom to the olefin ($n \rightarrow \pi^*$) and subsequent polarization or dissociation of the S–Cl bond with the formation of a cyclic transition state **21**.[64–66]



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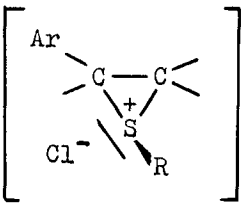


21

The formation of **20** and **21** has been confirmed by an analysis of the relative enthalpies of solvation of activated complexes in reactions of dimethoxyphosphoryl- and benzenesulfenyl chloride with styrene in various solvents.[62,67] With increasing solvating properties of the medium the addition rates are found to sharply increase in both reaction series: for the *P*-sulfenyl chloride and for PhSCl the replacement of hexane by acetonitrile results in a rise of k by a factor of 7500 and 5×10^6, respectively.[62]

In accordance with the Arnett approach,[68,69] dissolution heats ($\Delta H_{solv.}$) of sulfenyl chlorides and styrene[62] have been determined by a calorimetric method. Hence, according to the Arnett equation

$$(\delta H^{\neq}_{solv.})^{S}_{S_0} = (\Delta H^{\neq}_{S} - \Delta H^{\neq}_{S_0}) + \sum (\delta H^{init.}_{solv.})^{S}_{S_0},$$

where $(\delta H^{\neq}_{solv.})^{S}_{S_0}$ is the relative enthalpy of the solvation of the transition state in solvent

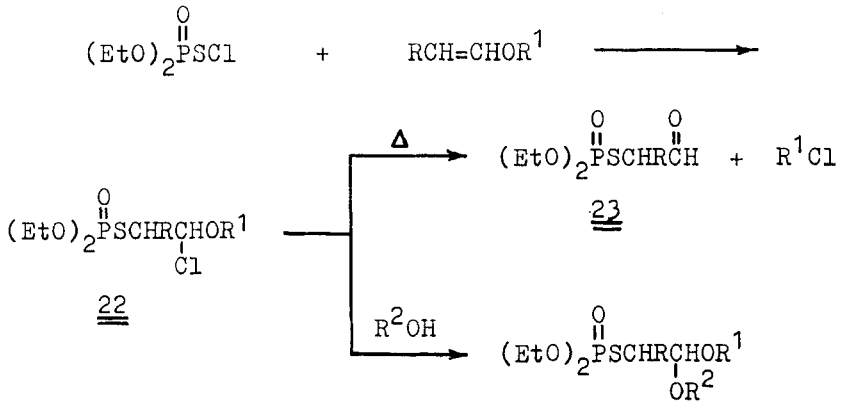
S in comparison with a standard solvent S_0 (benzene); $\Delta H_S^{\neq}$, $\Delta H_{S_0}^{\neq}$ are the enthalpies of activation in the solvents S and S_0; $\Sigma\ (\delta H_{solv.}^{init.})_{S_0}^{S}$ is the total enthalpy of solvation of the reagents; the relative enthalpies of the solvation of transition state in various solvents have been calculated.

If the transition state **20** is operative where the S–Cl bond preserves its covalent character and, in general, the structure of the activated complex does not differ much from that of the initial reagents, a linear dependence of $(\delta H_{solv.}^{\neq})_{S_0}^{S}$ on $\Sigma\ (\delta H_{solv.}^{init.})_{S_0}^{S}$ must be observed. The ionization of the S–Cl bond as in **21** will either impair or completely disrupt this correlation.

It has been found that this relationship has a linear character only for the reaction of the *P*-sulfenyl chloride with styrene; in the case of PhSCl, the correlation is not observed.[62] A proportionality factor of more than a unity for the Ad_E reaction of the *P*-sulfenyl chloride ($\rho = 2.4$) is indicative of the fact that during the formation of the activated complex **20** a noticeable change in the electronic situation in the initial compounds is observed, i.e. a considerable charge transfer from the olefin π-system to the electrophile. The conformation of the *P*-sulfenyl chloride with a *trans*-position of the P=O and S–Cl bonds also favors the structure **20** with the P=O group participating in the stabilization of a partial positive charge. The barrier of rotation around the P–S bond (> 42 kJ/mol) is considerably higher than the activation energy of the chlorothiophosphorylation of styrene ($\Delta H^{\neq}$ 13–28 kJ/mol).[17,62]

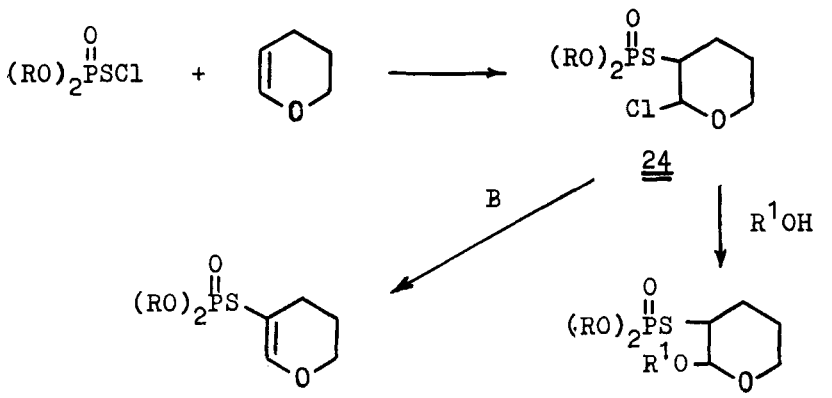
5. REACTIONS WITH UNSATURATED ETHERS AND SULFIDES

Reactions of dialkoxyphosphorylsulfenyl chlorides with alkyl vinyl ethers have been widely investigated;[13,43] the reaction proceeds under mild conditions (−20 −0 °C, solvent) with quantitative formation of the *O,O*-dialkyl-*S*-(2-chloro-2-alkoxyalkyl)thiophosphates **22**. The chlorine atom in the adduct **22** is rather mobile and may be easily substituted by another nucleophilic group. Upon heating of the reaction mixture the α-chloro ethers **22** eliminate alkyl chloride and transform into the thiophosphorylated aldehydes **23**.[13]



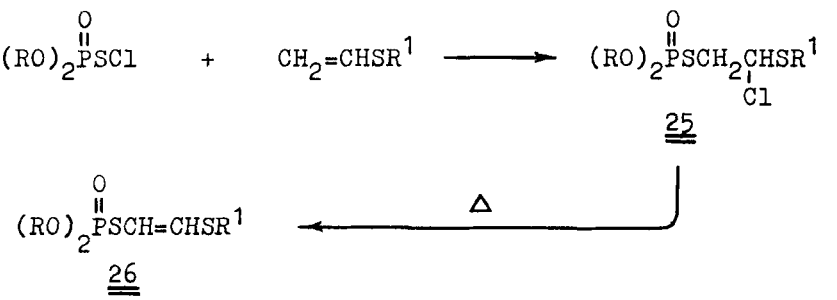
R = H, Ph; R^1 = Et, Bu; R^2 = alkyl

The interaction of *P*-sulfenyl chlorides with dihydropyran[73] proceeds in a similar way. The adduct **24** is labile and easily subject to dehydrochlorination under the action of triethylamine and even trialkyl phosphate.



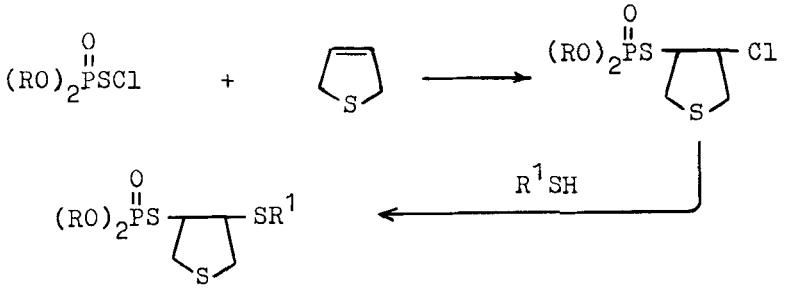
B = Et_3N, $(RO)_3P$

The lability of the chlorine atom in the reaction products of *P*-sulfenyl chlorides with unsatured sulfides is even higher.[16] A quantitative yield of *O,O*-dialkyl*S*-(2-alkylthiovinyl) thiophosphates **26** can be reached already upon heating of the α-chloro sulfides **25** *in vacuo*.[74]

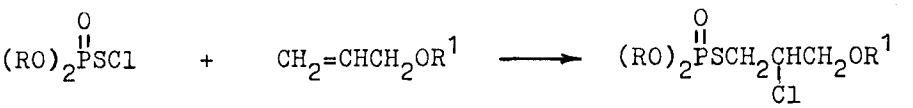


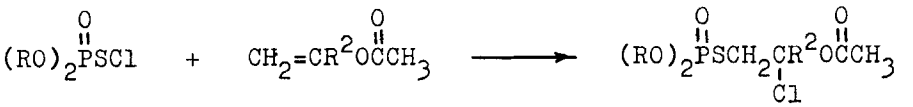
R = alkyl; R' = CH_3, C_2H_5, CH_2=CH

The chlorothiophosphorylation of 2,5-dihydrothiophene also proceeds under mild conditions.[75,76] The adducts **27** are easily subject to subsequent transformations.



Phosphorylsulfenyl chlorides add regioselectively to allyl alkyl ethers[77] and to vinyl carboxylates.[13,43]

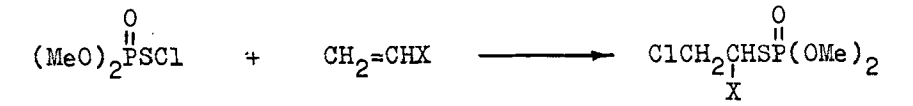




R,R^1 = alkyl; R^2 = H, CH_3

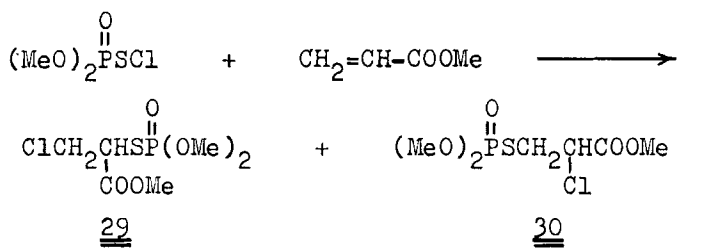
6. REACTIONS WITH UNSATURATED ORGANIC ELECTROPHILIC SYSTEMS

Dialkoxyphosphorylsulfenyl chlorides are capable of adding to unsaturated systems containing electron-withdrawing substituents. The reactions with acrylonitrile and methyl vinyl sulfone proceed regioselectively at -20 – $0\,^{\circ}C$ without solvent and produce the thiolophosphates **28**.[17]

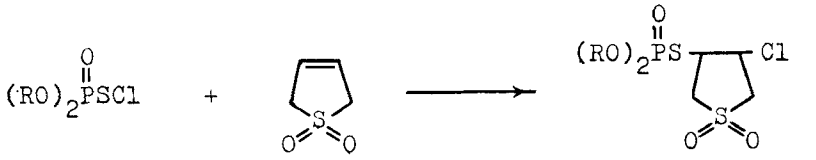


X = CN, SO_2Me

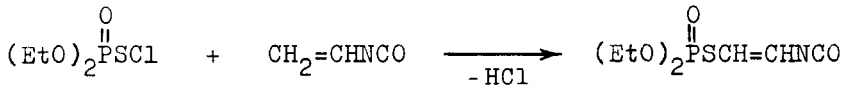
The interaction with methyl acrylate results in a mixture of the regioisomers **29** and **30** in a ratio of 1 : 2.[17]



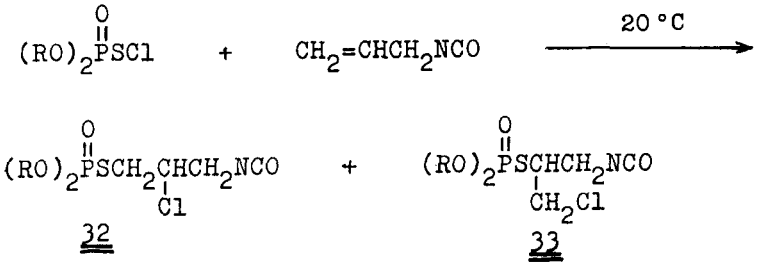
The reaction of *P*-sulfenyl chlorides with 3-sulfolene proceeds under somewhat more forcing conditions.[78] The adducts **31** have a pronounced pesticidal effect.



Adducts of *P*-sulfenyl chlorides and vinyl isocyanate undergo a ready dehydrochlorination. Formation of *O,O*-dialkyl *S*-(2-isocyanatovinyl) thiophosphates is observed.[79]

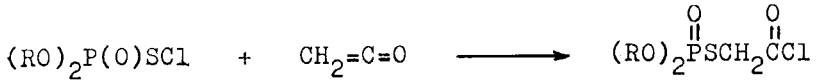


In the corresponding reaction with allyl isocyanate a mixture of the regioisomers **32** and **33** in the ratio 3 : 1 was obtained.[80]



R = Me, *i*-Pr

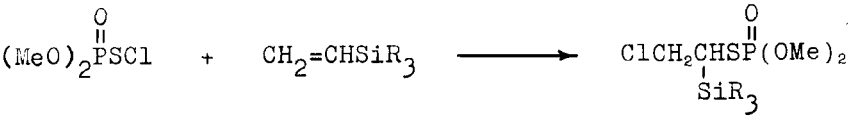
It has been shown that thiophosphorylsulfenyl chlorides are capable of adding to ketene.[15]



7. REACTIONS OF *P*- AND *C*-SULFENYL CHLORIDES WITH UNSATURATED ORGANOSILICON COMPOUNDS

7.1. With Vinylsilanes. Kinetics and Mechanism

Dialkoxyphosphorylsulfenyl chlorides are capable of easy addition to vinylsilanes, giving a high yield of the *O,O*-dialkyl *S*-(1-silyl-2-chloroethyl) thiophosphates **34**.[17,81,82]



R = Me, Et, Ph, PrO, *i*-PrO, PhO

The regiochemistry does not depend on the reaction temperature (−20 − 30 °C) and reagent ratio. The adducts **34** are thermodynamically stable and do not undergo regioconversion.

Organylsulfenyl chlorides can also form stable β-chloro adducts **35** upon reaction with silylethylenes.[82,83]

$$RSCl + CH_2{=}CHSiR^1_3 \longrightarrow ClCH_2\underset{\underset{SR}{|}}{C}HSiR^1_3$$

R = aryl; R^1 = alkyl, aryl, AlkO, ArO, Cl

On the basis of a kinetic study of the reactions of dimethoxyphosphoryl- and benzenesulfenyl chloride with vinylsilanes it has been established that the rate constants of these processes can be described by a second-order equation whereas the reagents are described by a first order equation.[82] With increasing electron-donor character of the *Si*-substituents the reaction rate increases (Ad_E, mechanism). The sensitivity of variable groups contained in the vinylsilane to inductive, resonance and steric effects is somewhat higher in the reaction with PhSCl than in that with *P*-sulfenyl chloride.

$(MeO)_2P(O)SCl$

$$\lg k = -1.71 - 1.91 \Sigma \sigma_I - 0.51 \Sigma \sigma_R$$

$$R = 0.960; S_0 = 0.262; n = 8$$

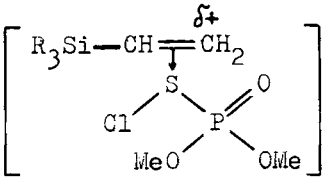
(the contribution made by the steric effect R_S[84] can be neglected).

PhSCl

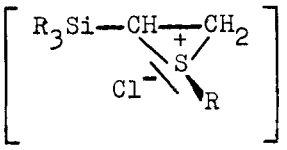
$$\lg k = -0.18 - 2.35 \Sigma \sigma_I - 0.89 \Sigma \sigma_R + 0.0016 \Sigma R_S$$

$$R = 0.970; S_0 = 0.414; n = 8$$

Such a difference in the parameters of the correlation equations is obviously associated with different symmetries of the cyclic activated complexes **36** and **37** formed in the rate-limiting steps. The presence of a bulky silyl group in the substrate promotes preferential bonding of the sulfur atom of the *P*-sulfenyl chloride to the α-carbon atom and the formation of a partial positive charge at the terminal olefinic carbon atom. The phosphoryl group is oriented in such a way that it ensures the most advantageous steric disposition of the π-complex **36** and stabilization of the incipient β-carbenium center.



36



37

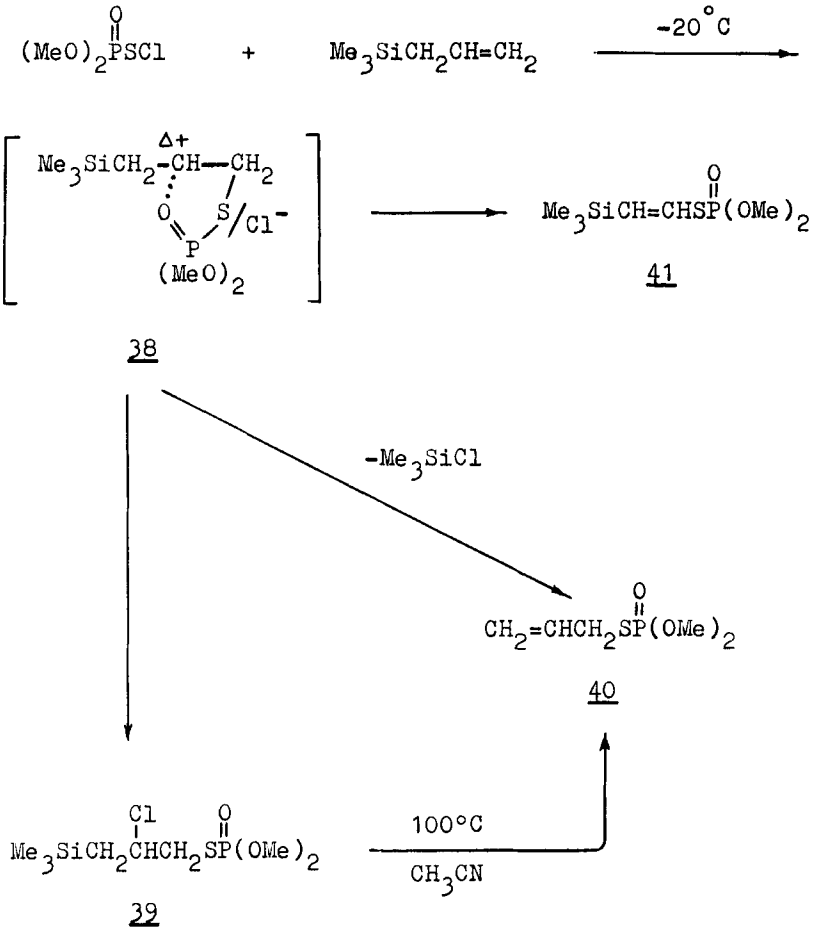
In reactions with PhSCl, the n-donor properties of the sulfur atom of which are rather high, the transition state has the more symmetric structure **37**. Therefore, there is also a lack of electron density at the α-carbon atom of the vinyl group and the aromatic ring is positioned not too far from the silyl group. This leads to a higher sensitivity of the reaction to the electronic and steric effects of the substituents in the silyl group compared to the addition of the *P*-sulfenyl chloride.

Investigations of the kinetics and the thermochemistry of the reactions of dimethoxy-

phosphoryl- and benzenesulfenyl chloride with vinylsilanes in various solvents showed that, similar to the reaction with styrene,[62] the relationship of the solvation enthalpies of the transition state and the starting materials is linear only in the case of the *P*-sulfenyl chloride.[82,85] For PhSCl this correlation is absent. Thus, when the *P*-sulfenyl chloride is activated the S–Cl bond maintains its covalent nature (**36**). It is considerably ionized in the transition state (**37**) with the participation of benzenesulfenyl chloride.

7.2. With Allyl- and 3-Butenylsilanes

The interaction of *P*-sulfenyl chlorides and allylsilanes follows several pathways. As a result of the reaction of dimethoxyphosphorylsulfenyl chloride with allyltrimethyl silane *O,O*-dimethyl *S*-allyl thiophosphate **40** and (*E,Z*)-*O,O*-dimethyl *S*-(3-trimethylsilyl-2-propenyl) thiophosphate **41** in the ratio 3 : 1 : 2 (Scheme 3)[86] were obtained and individually characterized.

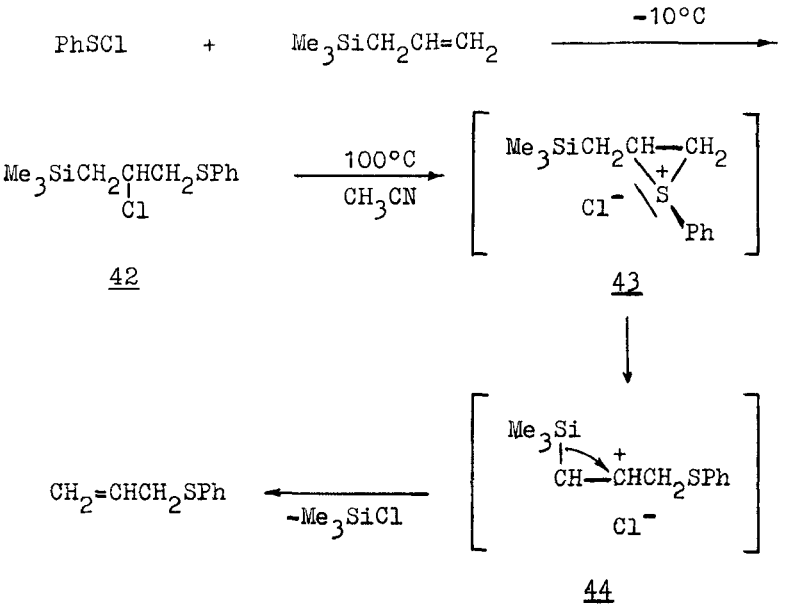


Scheme 3.

All three reaction pathways are operative at the same time and this has been proven by specific experiments. The adduct **39** is thermally stable and only upon heating in a polar solvent it loses trimethylchlorosilane and forms the allyl thiophosphate **40**. Dehydrochlorination of the thiophosphate **39** does not take place, not even under the action of triethylamine. Thus, under the reaction conditions (−20 °C, CCl_4), the adduct **39** is not a precursor of the thiolophosphates **40** and **41**.

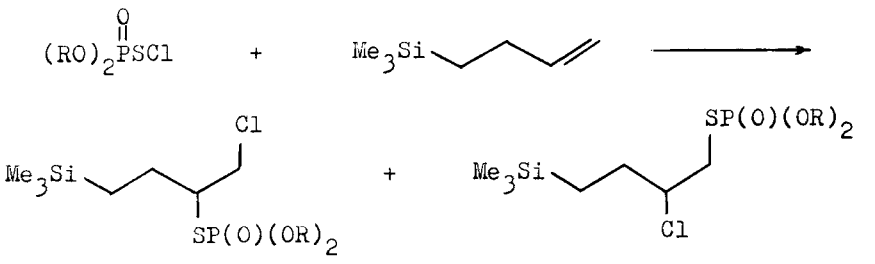
It can be assumed that the initially formed carbenium type intermediate **38** which produces adduct **39** according to the conventional Ad_E mechanism is also capable of stabilization by elimination of the trimethylsilyl group and formation of the *S*-allyl thiophosphate **40**. After deprotonation a mixture of the *Z*,*E*-isomers of the unsaturated thiophosphate **41** is obtained.

Benzenesulfenyl chloride reacts with allyltrimethylsilane exclusively along the addition pathway and forms the rather stable (3-phenylthio-2-chloropropyl)trimethylsilane **42**.[86] However, upon heating in a polar solvent, **42** decomposes to allyl phenyl sulfide and trimethylchlorosilane. This fact indicates the possibility of the conversion of the episulfonium intermediate **43** into the carbenium ion **44** with subsequent elimination of the Me_3Si group (Scheme 4),



Scheme 4.

If a silicon atom is separated from an unsaturated reaction center by two methylene groups its part in the reaction with *P*-sulfenyl chlorides is not particularly important. Dialkoxyphosphoryl(thiophosphoryl)sulfenyl chlorides add quantitatively to 3-butenyltrimethylsilane and produce a mixture of the isomeric adducts **45** and **46** (Scheme 5).[86]



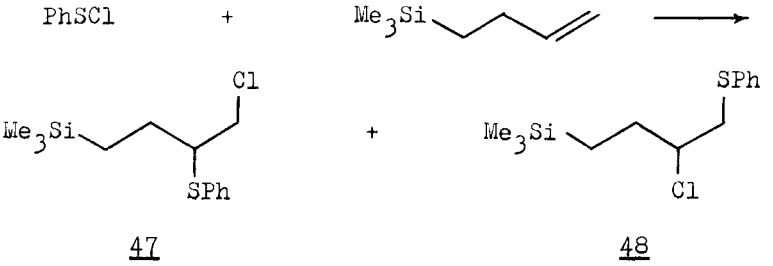
45 46

R	X	45 : 46
Me	O	10 : 1
i-Pr	S	15 : 1

Scheme 5.

The compounds **45** and **46** are resistant to heat, even in a polar solvent (100 °C, CH_3CN, 20 h).

The interaction of benzenesulfenyl chloride with 3-butenyltrimethylsilane also results in a mixture of the adducts **47** and **48**.[86] When heated in CH_3CN **47** forms the thermodynamically more stable isomer **48** (Scheme 6).

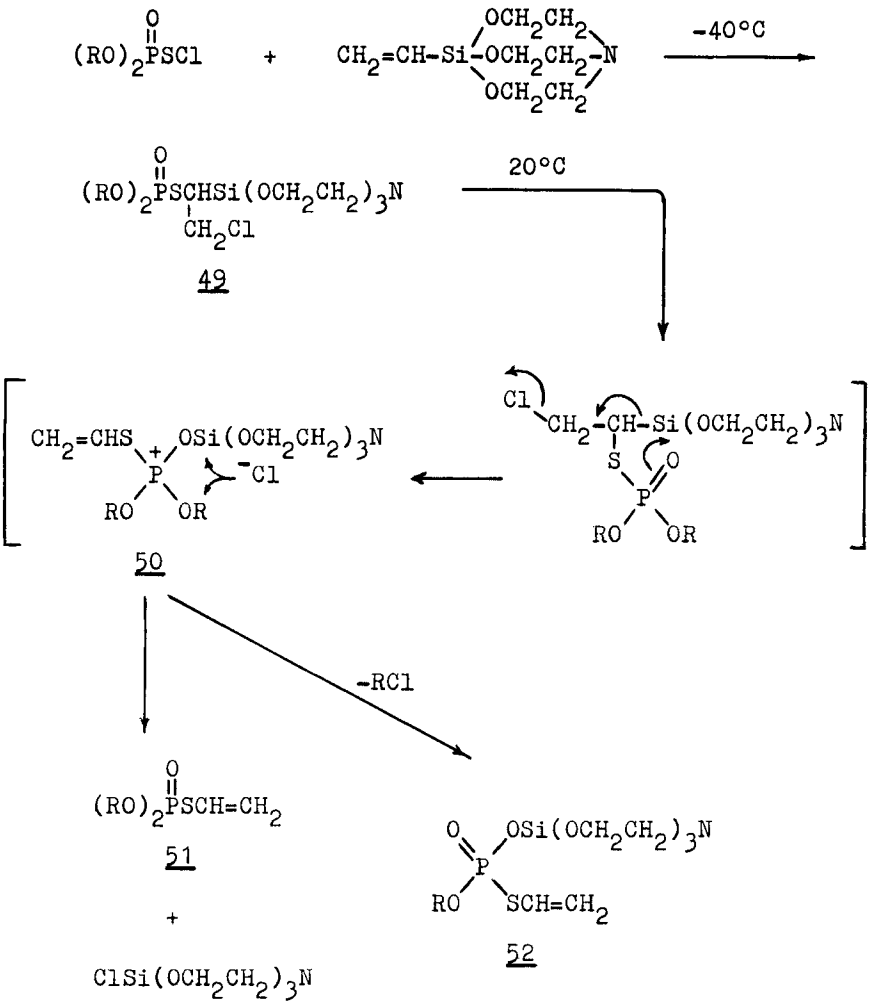


47 48

Scheme 6.

7.3. With Vinyl- and Allylsilatranes

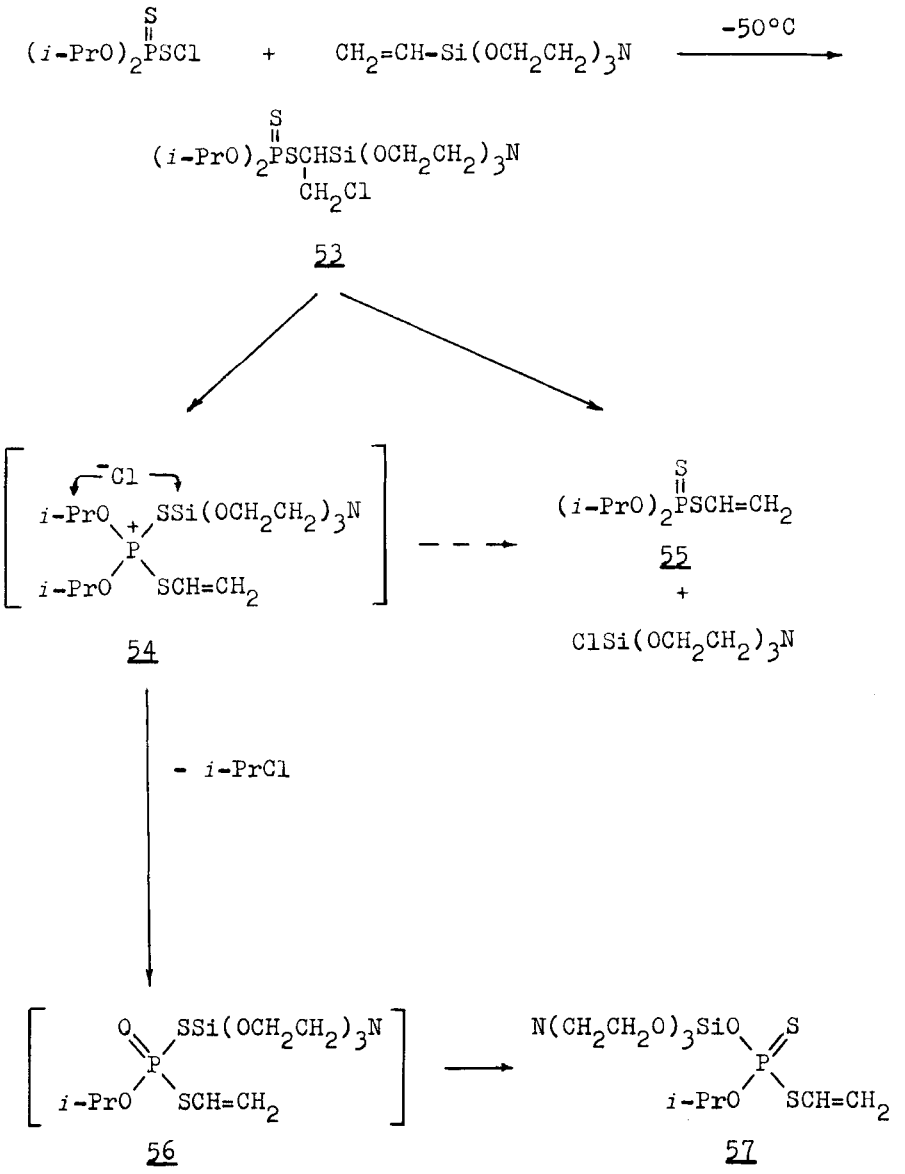
Dialkoxyphosphorylsulfenyl chlorides react with vinylsilatrane already at −40 °C, giving quantitatively the *O,O*-dialkyl *S*-(1-silatranyl-2-chloroethyl) thiophosphates **49**.[87,88] The adducts **49** are unstable and during several hours at 20 °C they decompose completely along two pathways. Elimination of chlorosilatrane produces the *O,O*-dialkyl *S*-vinyl thiophosphates **51**; dechloroalkylation combined with C→O migration of the silatranyl group results in the *O*-alkyl *O*-silatranyl *S*-vinyl thiophosphates **52** (Scheme 7). The simultaneous formation of **51** and **52** proves that chlorosilatrane is incapable of dealkylating the *S*-vinyl thiophosphates **51** and, therefore, this interaction cannot be the cause of the formation of the *O*-silatranyl thiophosphates **52**.



R	51 : 52
Me	2 : 3
i-Pr	3 : 2

Scheme 7.

Since addition products of *P*-sulfenyl chlorides to acyclic vinylsilanes are rather stable,[17,81,82] the ease of the fragmentation of **49** is, evidently, determined by the strong electron-donor effect of the silatranyl group ($\sigma^* = -0.9$[89]) based on a transannular N → Si interaction[90] which facilitates the elimination of a chloride anion. As a result of the migration of the silatranyl group to the phosphoryl oxygen a quasi-phosphonium



Scheme 8.

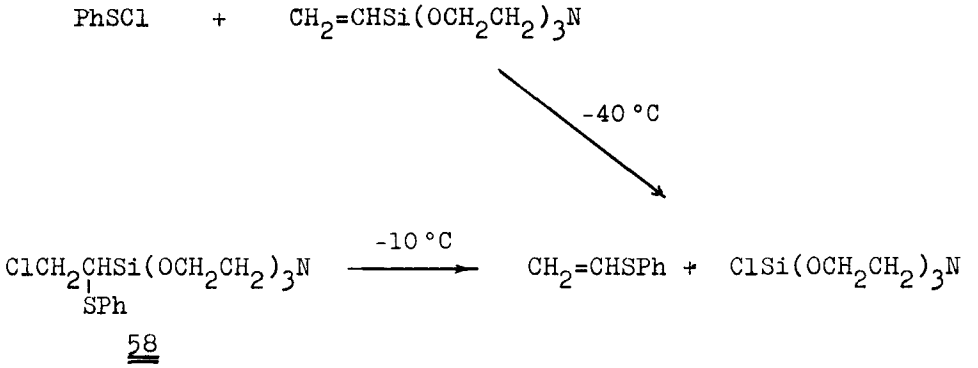
intermediate **50** is formed which decomposes according to the second stage of the Arbuzov reaction along two pathways. Here, increasing bulk of a *P*-alkoxy group (replacement of Me by *i*-Pr) impedes the dealkylation process: the ratio of the thiolophosphates **51** : **52** changes in favor of the S-vinyl thiophosphate **51**.[87]

At the same time one cannot exclude the possibility of the formation of the vinyl thiophosphates **51** directly from **49** circumventing the formation of the quasi-phosphonium intermediate **50**, since the capability of 2-chloroethylsilanes to undergo

β-decay is well known, its ease increases with increasing electron-donor properties of the substituents at the silicon atom.[91]

The replacement of the phosphoryl group in the *P*-sulfenyl chloride by a thiophosphoryl group brings some changes in the character of the process. The reaction of diisopropoxythiophosphorylsulfenyl chloride with vinylsilatrane at first also results in **53**, an *S*-(1-silatranyl-2-chloroethyl) dithiophosphate.[88,92] However, the primary pathway of its stabilization is the elimination of chlorosilatrane and formation of the *S*-vinyl dithiophosphate **55** and this phenomenon is probably associated with the lower energy of the Si-S bond compared to Si-O.[93] On one hand this impedes the Si→S migration of the silatranyl group to the thiono sulfur atom. On the other hand it facilitates cleavage of the Si-S bond in the quasi-phosphonium intermediate **54** under the action of a chloride anion. The dealkylation product of the intermediate **54** is labile and, like all *S*-silyl ethers of phosphorus thioacids,[94] it rapidly isomerizes to the *O*-silatranyl dithiophosphate **57** (Scheme 8).[88,92]

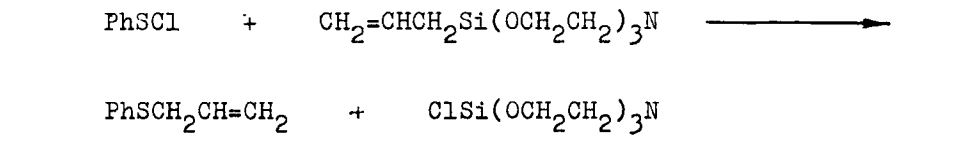
In the reaction of benzenesulfenyl chloride with vinylsilatrane the initially formed adduct **58** above −10 °C completely decomposes to vinyl phenyl sulfide and chlorosilatrane.[87]

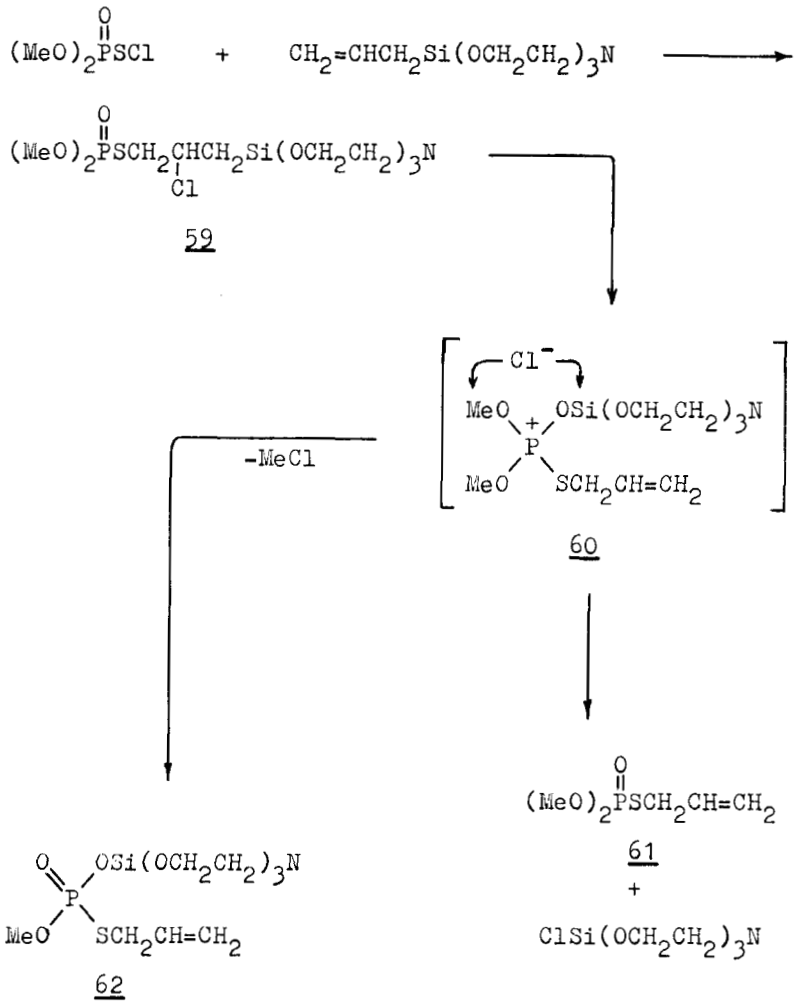


58

Upon interaction of dimethoxyphosphorylsulfenyl chloride with allylsilatrane *O,O*-dimethyl *S*-allyl thiophosphate **61**, chlorosilatrane, *O*-methyl *O*-silatranyl *S*-allyl thiophosphate **62** and methyl chloride are obtained.[87,92] The ratio **61** : **62** is 1 : 1. This process is evidently similar to the corresponding reaction with vinylsilatrane and involves the intermediate **59** which decomposes via the quasi-phosphonium salt **60** (Scheme 9).

Benzenesulfenyl chloride reacts with allylsilatrane, yielding allyl phenyl sulfide and chlorosilatrane.[87]





Scheme 9.

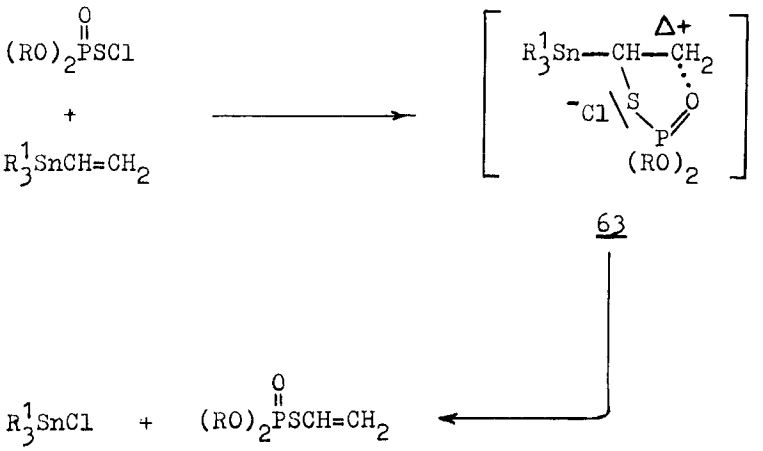
8. REACTIONS OF *P*- AND *C*-SULFENYL CHLORIDES WITH UNSATURATED ORGANOTIN COMPOUNDS

8.1. With Vinyl- and Allylstannanes

Reactions of dialkoxyphosphorylsulfenyl chlorides with vinyltrialkylstannanes result in *O,O*-dialkyl *S*-vinyl thiophosphates and trialkylchlorostannanes.[86,95] Adducts are not observed, not even at low temperatures (−65 °C) (Scheme 10).

Upon interaction of arenesulfenyl chlorides with vinylstannanes both the adducts **65** and the substitution products **66** (Scheme 11) have been obtained.[96,97]

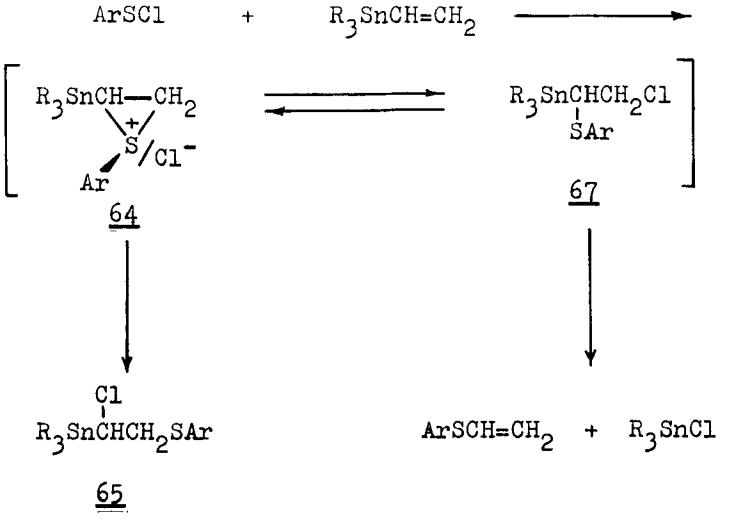
The relative amount of **65** (30–70%) increases upon replacement of the methyl groups at the tin atom by phenyl groups and decreases with increasing electron-donor properties of the substituents in the aromatic ring of the electrophile.[97]



Scheme 10.

We assume that the cause of the different courses of the reactions of *P*- and *C*-sulfenyl chlorides with vinylstannanes is a difference in the structure of the intermediates, as in the reactions with alkenylsilanes.[86] In the reaction with *P*-sulfenyl chlorides a carbonium type intermediate **63** (Scheme 10) is formed in which a partial positive charge is located mainly at the terminal carbon atom. Here, there is a possibility of stabilization of the partial positive charge by means of (σ-p) conjugation with an Sn–C bond and coordination with the phosphoryl oxygen promotes a favorable steric orientation of bulky stannyl and phosphorus groups. This structure of the intermediate **63** leads to fast elimination of the organotin fragment.

For arenesulfenyl chlorides elimination of the R_3Sn group from the cyclic inter-



Scheme 11.

mediate **64** is difficult due to the orthogonal positions of the σ-orbitals of the Sn–C and C–S bonds (Scheme 11).[83] Therefore, opening of the episulfonium ring takes place under the influence of the chloride anion which leads to the adducts **65** and **67**. The absence of the β-chloroorganylstannane **67** in the reaction mixture can be explained by its rapid decay with elimination of a chlorostannane.[97]

Allylstannanes react with phosphoryl-[86] and arenesulfenyl chlorides[96] only with cleavage of an Sn–C bond. In both processes, even at $-65\,^{\circ}C$, no adducts have been found.

$$RSCl + CH_2{=}CHCH_2SnMe_3 \xrightarrow{-65\,^{\circ}C} RSCH_2CH{=}CH_2 + ClSnMe_3$$

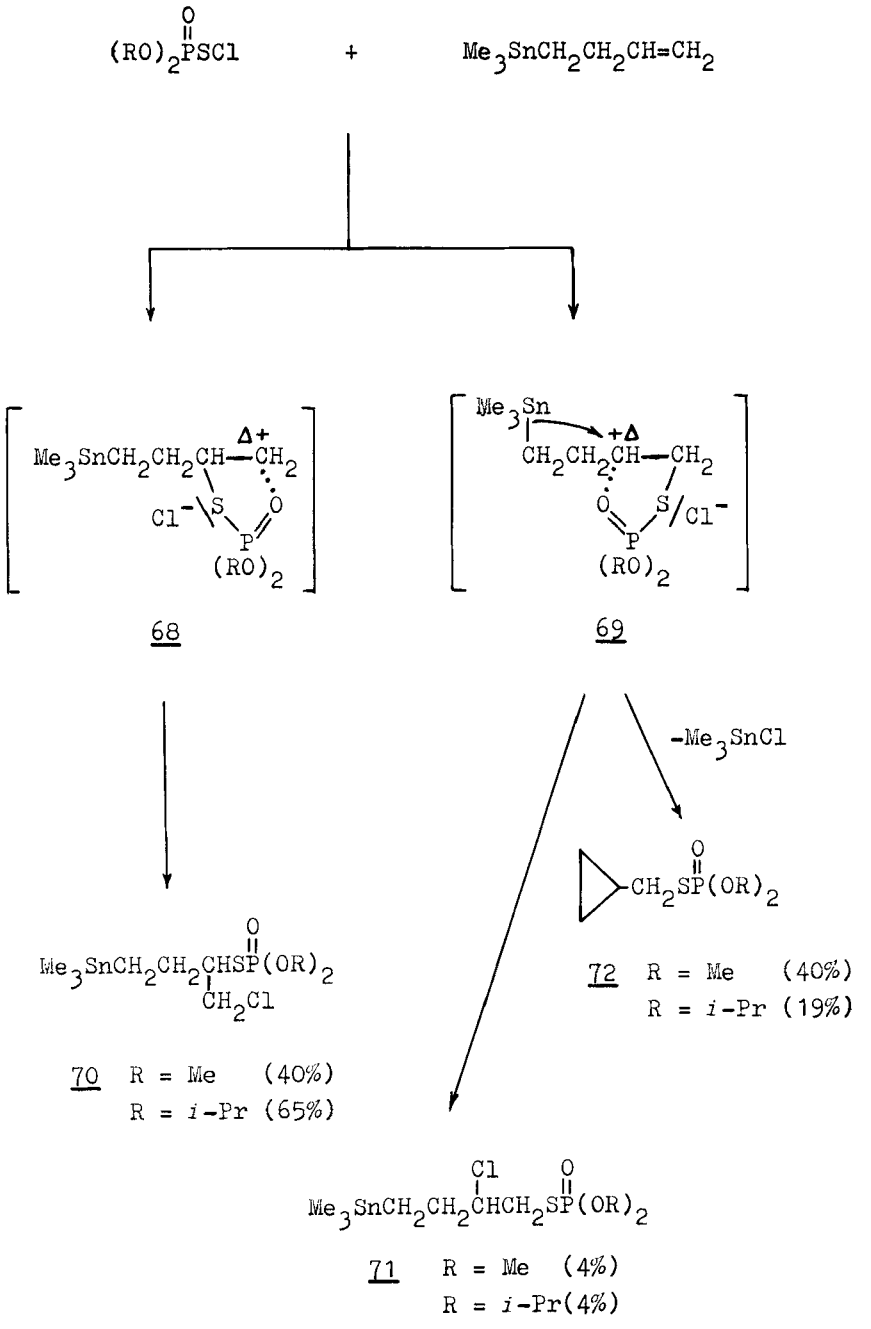
$$R = (MeO)_2P(O),\ Ph$$

However, evidently the interaction of *P*- and *C*-sulfenyl chlorides with allylstannanes proceeds with participation of a π-system of the substrate, similar to the corresponding reactions with phenyltin derivatives. This is proven by the kinetic data of the S_E reactions of phosphoryl- and benzenesulfenyl chloride with tetraalkylstannanes.[95] It has been shown that the reaction rates of sulfenyl chlorides with tetraalkyl-, alkylaryl- and trialkylbenzylstannanes is considerably lower than those with unsaturated organotin compounds. The replacement of the vinyl group in trimethylvinylstannane for a more nucleofugal, though less pronounced π-donor group, phenylethylnyl (Me_3Sn-C≡C-Ph), also decreases noticeably (by a factor of 100) the rate of the S_E process.[95]

8.2. With 3-Butenylstannanes

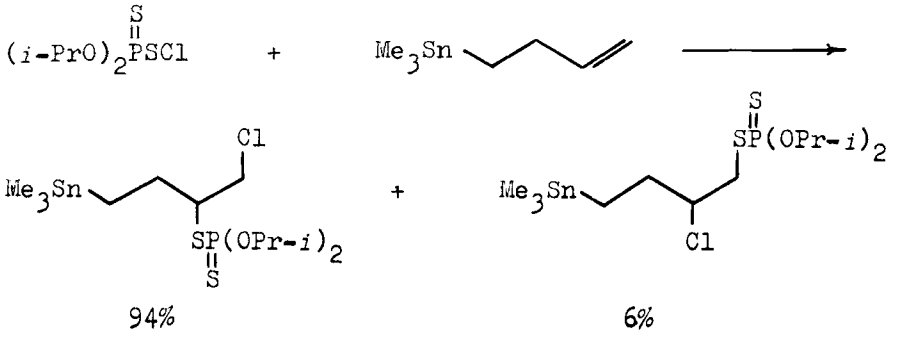
The introduction of a methylene group between the σ- and π-centers (Sn–C and C=C bonds) of the alkenylstannane changes substantially the character of the reaction. Dialkoxyphosphorylsulfenyl chlorides react with 3-butenyltrimethylstannane and form, along with the adducts **70** and **71**, the *O,O*-dialkyl *S*-cyclopropylmethyl thiophosphates **72**.[86] The adducts **70** and **71** are thermally stable and neither isomerize, nor do they eliminate trimethylchlorostannane, even at a high temperature in a polar solvent (100 °C, CH_3CN, 20 h), i.e. the formation of the thiophosphates **70–72** takes individual routes (Scheme 12).

For the reaction with dimethoxyphosphorylsulfenyl chloride the probability of the formation of the intermediates **68** and **69** is equal, the ratio of thiophosphates **70** : (**71** + **72**) is about 1 : 1. The preferential route of stabilization of the intermediate **69** is a cyclodestannylation process (**72** : **71** = 10 : 1). With increasing bulk of the alkoxy groups at the phosphorus atom (Me → *i*-Pr), the formation of the intermediate **68** where bulky substituents are at a distance, becomes even more advantageous. The relative amount of **70** in the reaction mixture increases, **70** : (**71** + **72**) = 3 : 1. Here, the main transformation of intermediate **69** is a pathway leading to the *S*-cyclopropylmethyl thiophosphate **72** (**72** : **71** = 5 : 1) (Scheme 12).

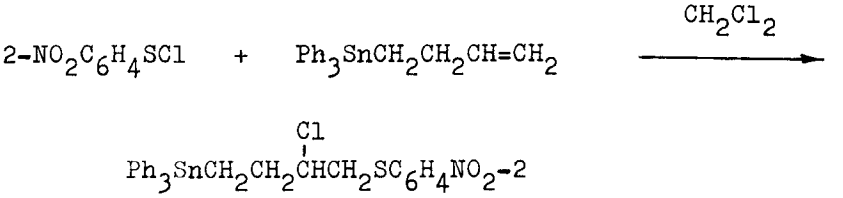


Scheme 12.

The substitution of the phosphoryl group in the sulfenyl chloride by thiophosphoryl hardly affects the ratio of adducts formed; however, the cyclodestannylation process is almost completely suppressed.[86]



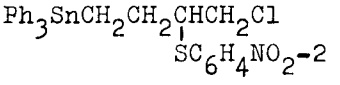
The results of investigations of reactions of arenesulfenyl chlorides with 3-butenylstannanes are rather contradictory. In the overwhelming majority of cases only aryl cyclopropylmethyl sulfides[98-100] were obtained. No adducts were observed and it was therefore assumed that the elimination of the stannyl group and the closing of the cyclopropane ring occur immediately after the C=C double bond has been attacked by the sulfenyl chloride.[98,99] Only in the reaction of 2-nitrobenzenesulfenyl chloride with 3-butenyltriphenylstannane the thermally stable 4-(triphenylstannyl)-3-chlorobutyl 2-nitro-phenyl sulfide **73** was obtained.[101]



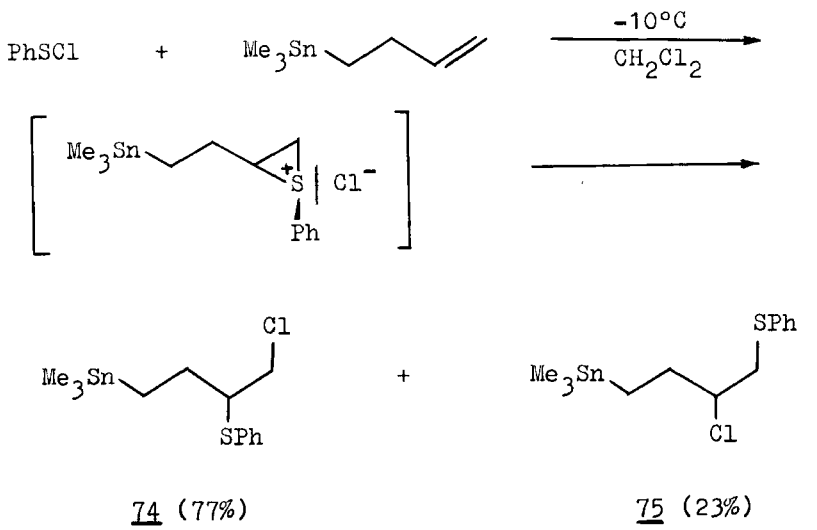
73

However, a detailed investigation of the reaction of benzenesulfenyl chloride with 3-butenyltrimethylstannane, performed by means of ^{1}H and ^{13}C NMR spectroscopy, showed that the reaction products are the isomeric sulfides **74** and **75** the ratio of which remains unchanged after vacuum distillation (Scheme 13).[86]

The comparison of the ^{13}C NMR spectral characteristics of the adducts **73**, **74** and **75** unambiguously shows that structure **73** has erroneously been ascribed to the product of butenyltriphenylstannane chlorosulfenylation. The isomeric sulfide **76** has been obtained by the authors.[101]

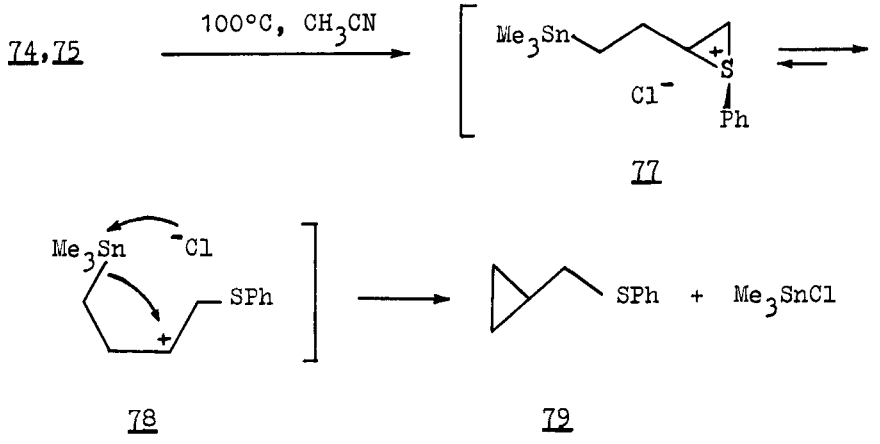


76



Scheme 13.

Prolonged heating of **74** and **75** in CCl_4 (100 °C, 6 h) does not lead to any transformations; however, compound **74** isomerizes to the thermodynamically more stable 4-(trimethylstannyl)-2-chlorobutyl phenyl sulfide **75** in a polar solvent (CH_3CN, 100 °C, 0.5 h). In the course of the reaction a partial dechlorostannylation of the adducts and formation of cyclopropylmethyl phenyl sulfide **79** is observed. Prolonged heating (CH_3CN, 100 °C, 3 h) results in complete transformation of the sulfides **74** and **75** to the sulfide **79** with elimination of trimethylchlorostannane (Scheme 14).[86]



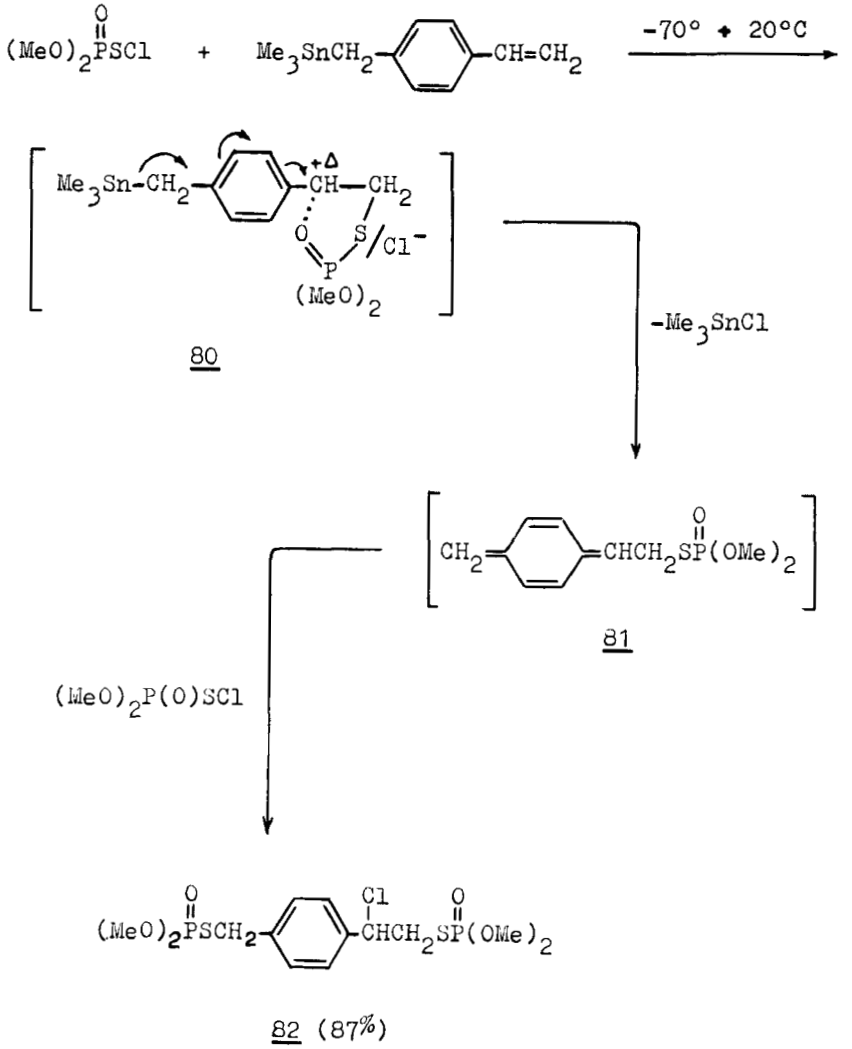
Scheme 14.

Evidently, under these conditions (polar solvent, high temperature) the adducts **74** and **75**, as a result of nucleophilic substitution of the chlorine atom by sulfur, are converted to the episulfonium ion **77** which decomposes irreversibly via the more polar

carbenium ion **78** with further elimination of trimethylchlorostannane and closure of a cyclopropane ring.

8.3. With (4-vinylbenzyl)trimethylstannane

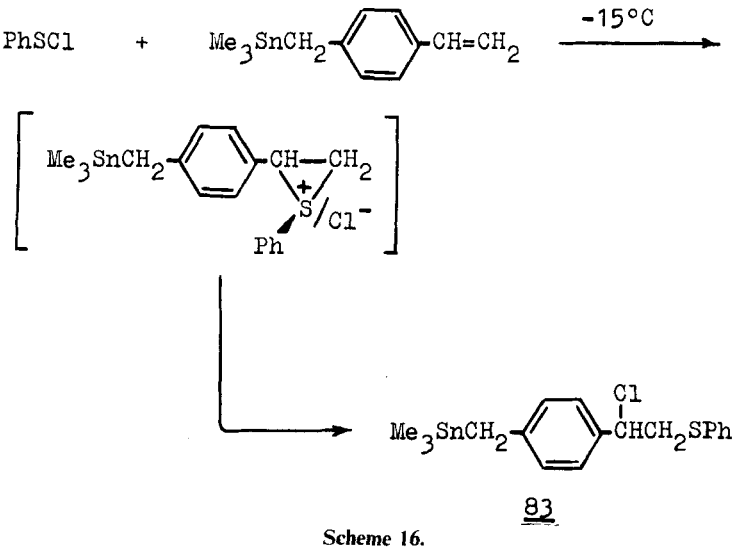
New interesting aspects of the reactivity of *P*-sulfenyl chlorides have been found in the reaction with (4-vinylbenzyl)trimethylstannane.[102] Irrespective of the temperature (−70 − 20 °C), the nature of the solvent (CCl_4, C_6H_6, $CHCl_3$, Et_2O) and the reagent ratio (2:1, 1:2), the only reaction product is *O,O*-dimethyl *S*-[2-(4-dimethoxyphosphorylthiomethyl)phenyl-2-chloroethyl] thiophosphate **82** (Scheme 15).



Scheme 15.

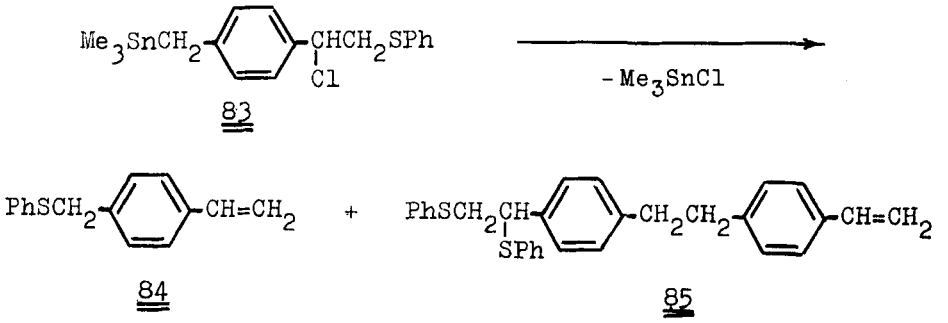
We believe that the electrophilic attack of phosphorylsulfenyl chloride takes place at the double bond of the unsaturated stannane, since under the above specified conditions benzyltrimethylstannane does not react with *P*-sulfenyl chlorides. A carbenium type intermediate **80** formed in the reaction eliminates the Me_3Sn group and transforms to the thiophosphorylated *p*-xylylene **81**. It is known that such compounds are prone to 1,6-addition reactions,[103] therefore, intermediate **81** rapidly reacts with a second molecule *P*-sulfenyl chloride and forms the bis-thiophosphate **82** (Scheme 15).

With the replacement of the phosphorus electrophile by benzenesulfenyl chloride (of which the formation of episulfonium type intermediates with a relatively small electron density deficiency at the carbon atoms of an unsaturated center is characteristic), the interaction with (4-vinylbenzyl)trimethylstannane proceeds only along the addition pathway[102] (Scheme 16).



Scheme 16.

Adduct **83** is fairly stable at 10 °C, however, at 20 °C it completely decomposes over 48 h (even in solution) with elimination of Me_3SnCl.[102] Among the products of this unusual 1,6-dechlorostannylation are 4-vinylbenzyl phenyl sulfide **84** and compound **85** the structures of which have been proven by NMR spectroscopy and mass spectrometry.

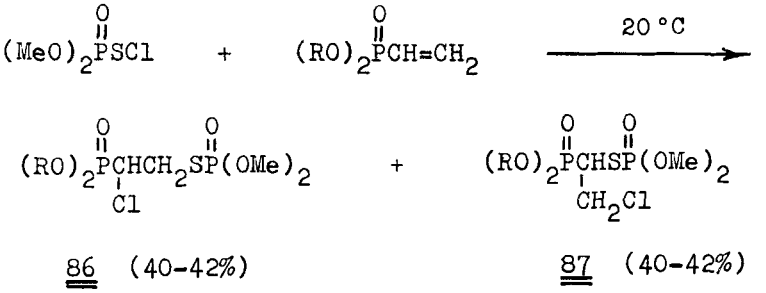


The fragmentation of adduct **83** evidently involves intermediate formation of phenylthiomethyl-*p*-xylylene, similar to intermediate **81**. Its rearrangement leads to 4-vinylbenzyl phenyl sulfide **84**, and dimerization, accompanied by migration of the PhS group, produces adduct **85**.

9. REACTIONS OF *P*- AND *C*-SULFENYL CHLORIDES WITH UNSATURATED ORGANOPHOSPHORUS COMPOUNDS

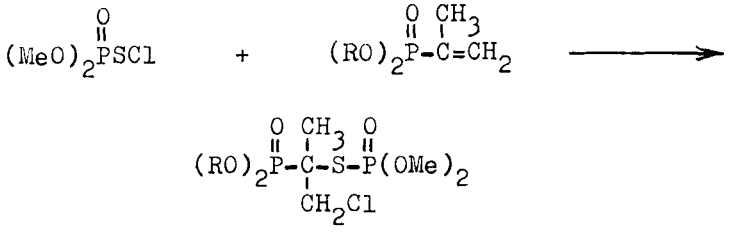
9.1. With Vinyl- and Isopropenylphosphonates

9.1.1. Regiochemistry The addition of dialkoxyphosphorylsulfenyl chlorides to vinylphosphonates results in the formation of mixtures of regioisomers.[17] The adducts **86** and **87** are thermodynamically stable and do not undergo subsequent isomerization.



86 (40–42%) **87** (40–42%)

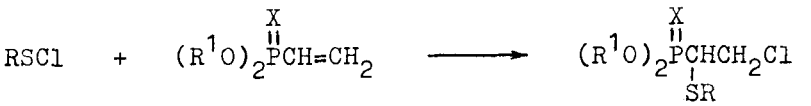
The reaction with isopropenylphosphonates proceeds regioselectively.[104]



74–82%

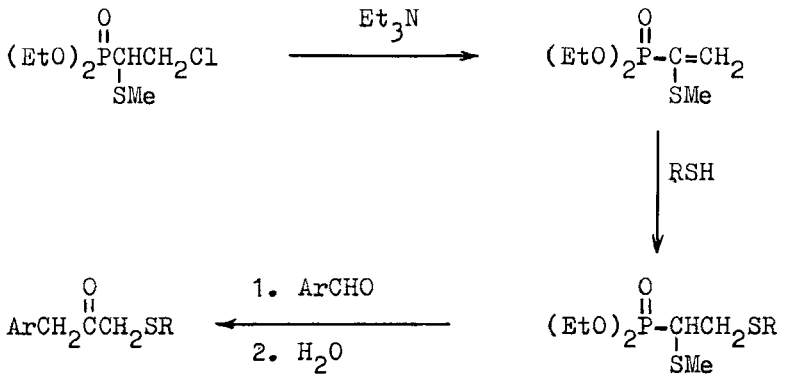
R = Me, *i*-Pr

It is believed that when ethane- and methanesulfenyl chloride react with dialkylvinylphosphonates and -thiophosphonates the unusual 1-alkylthio-2-chloroethylphosphonates (thiophosphonates) are formed.[105-107]

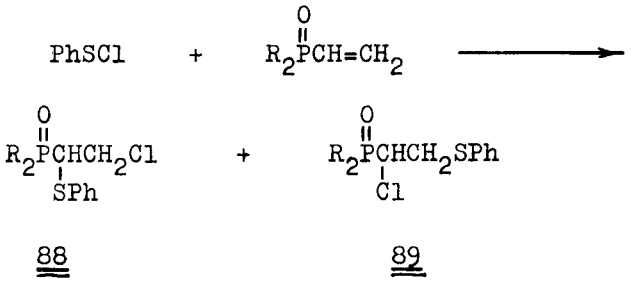


R = Me, Et; R^1 = alkyl; X = O,S

In the case of methanesulfenyl chloride, the reaction is used for the preparative synthesis of α-(alkylthio)ketones.[107]



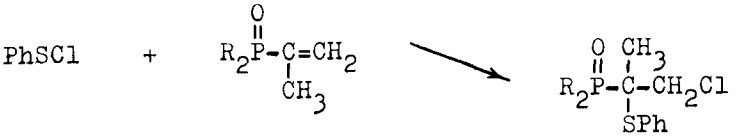
A thorough ^{1}H and ^{13}C NMR spectroscopic analysis of the reaction products from benzenesulfenyl chloride and vinylphosphonates showed that besides the 2-chloroethylphosphonates **88** the 1-chloro isomers **89** are also formed.[104,108] The adducts **89** gradually (25 °C, 2–3 weeks) transform to the more thermodynamically stable 2-chloroethylphosphonates **88**. The ratio of the regioisomers **88** and **89** estimated immediately after completion of the Ad_E process, shows that the relative amount of phosphonate **88** increases with a decreasing bulk of the substituents at the phosphorus atom and upon an increase of their electron-withdrawing properties.[104]



88 **89**

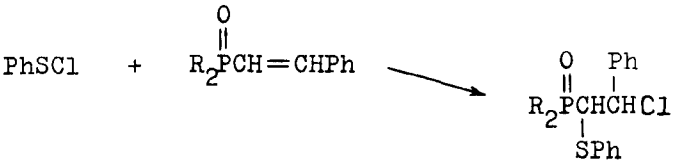
R	**88** : **89** %
i-C_3H_7O	70 : 30
C_2H_5O	80 : 20
R_2= $OCMe_2CMe_2O$	80 : 20
CD_3O	90 : 10
$ClCH_2CH_2O$	95 : 5
Cl	100 : 0

In the case of isopropenylphosphonate the α-carbon center of which is sterically shielded, the attack of the chloride anion in an unusual fashion takes place at the terminal carbon atom.[104,108]



R = MeO, *i*-PrO, Cl

The phenyl group contained in styrylphosphonates gives rise to a similar effect.[104]



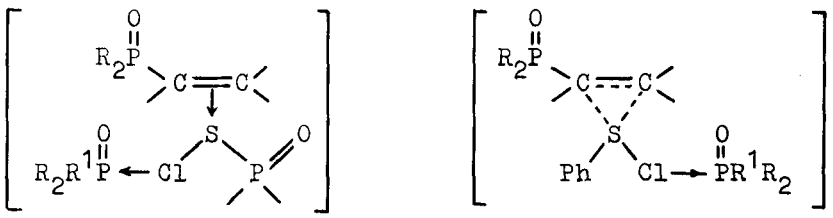
9.1.2. Kinetics and mechanism The investigation of the kinetics of the reactions of dimethoxyphosphoryl- and benzenesulfenyl chloride with vinyl- and isopropenylphosphonates has revealed a substantial dependence of the mechanism on the structure of the unsaturated compound and the nature of the solvent.[104,108] The reaction order with respect to the alkenylphosphonate changes from first to second with increasing electron-withdrawing effect of the substituents at the phosphorus atom in the substrate and decreasing solvating properties of the medium; the reaction order with respect to the sulfenyl chloride remains first.

In general, the rate of the Ad_E process can be described by equation (1)

$$V = K_2[P][S] + k_3[P]^2[S] \quad (1)$$

where k_2 and k_3 are rate constants of the second and third order, respectively; [P] and [S] are the concentrations of the unsaturated phosphonate and the sulfenyl chloride, respectively.

The appearance of a third-order component in equation (1) (Ad_{E3} mechanism) when the reaction proceeds in poorly solvating solvents (such as tetrachloromethane, benzene, chlorobenzene, dioxane, dichloroethane) can be explained by the participation in the reaction of a second molecule of alkenylphosphonate which stabilizes the transition states **90** and **91** of the first rate-determining step of the reaction at the expense of the coordination of the chlorine atom of the sulfenyl chloride with the phosphorus atoms of the unsaturated reaction partner. Such complexing promotes a polarization of the S–Cl bond and stimulates additional shift of electron density from the π-system of the alkenylphosphonate to the electrophile. This process is particularly important with unsaturated phosphorus compounds the ionization potential of which is sufficiently high (IP = 10.6–11.5 eV).[109]



90 91

R = AlkO, Cl; R^1 = CH_2=CH, CH_2=C(CH_3), AlkO, Cl

The reduced π-donor properties of the C=C double bond with increasing electron-withdrawing effect of the substituents at the phosphorus atom of the alkenylphosphonate results in increased importance of the Ad_{E^3} route.

Thus, the reaction of PhSCl with *O,O*-bis(2-chloroethyl) vinylphosphonate proceeds according to the Ad_{E^3} mechanism in media (CCl_4, C_6H_6) whereas the interaction with the stronger π-donor *O,O*-diethvinylphosphonate involves the Ad_{E^2} process as well (Table 2).[108]

The participation in the coordination of the phosphoryl group of the alkenylphosphonate is proven by the fact that the rate of chlorosulfenylation of vinylphosphonates increases in the presence of saturated phosphoryl compounds (such as phosphates, phosphonates, phosphorus acid chlorides) which themselves do not react with *P*- and *C*-sulfenyl chlorides.[104,108] The overall reaction rate in this system can be described by equation (2):

$$v = k_2[P][S] + k_3[P]^2[S] + k_3'[P][S][P'] \quad (2)$$

where [P] and [S] are the concentrations of the reagents; [P'] is the concentration of an additionally introduced phosphorus compound; k_2 and k_3 are the second- and third-order rate constants of the reaction of the alkenylphosphonate with the sulfenyl chloride; k_3' is the third-order rate constant of the reaction with participation of a saturated phosphorus compound.

The additional third term of equation (2) reflects the contribution of a new reaction pathway in which the functions of a catalyst are performed not by the second molecule of vinylphosphonate, but by the saturated phosphoryl compound. With increasing concentration of the phosphorus additive [P'] the importance of the second Ad_{E^3} route

Table II. Reaction Rate Constants RSCl + $(R^1O)_2P(O)CR^2=CH_2$ (25 °C)

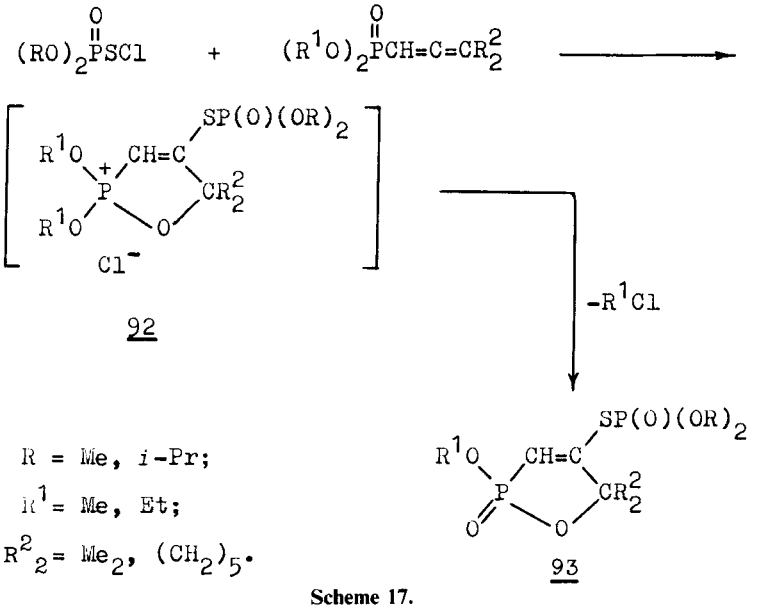
R	R^1	R^2	Solvent	$k_2 \times 10^3$ l/mol × sec	$k_3 \times 10^3$ l^2/mol^2 × sec
$(MeO)_2p(O)$	Et	H	C_6H_5CN	1.0	1.2
$(MeO)_2P(O)$	Me	Me	C_6H_5CN	–	0.56
Ph	Et	H	C_6H_5CN	20.2	–
Ph	Me	Me	C_6H_5CN	34.0	–
Ph	Et	H	C_6H_6	0.29	1.15
Ph	$ClCH_2CH_2$	H	C_6H_6	–	0.72

increases and the partial order of the reaction with respect to the alkenylphosphonate approaches unity.

As has been exemplified by the reaction of *P*-sulfenyl chlorides with styrene[62] and vinylsilanes,[82] for phosphorylsulfenyl chlorides the formation of a π-type activated complex **90** in the rate-limiting step is characteristic, together with the preservation of the covalent S–Cl bond. Therefore, when *P*-sulfenyl chlorides react with vinylphosphonates, the stabilizing effect of the complexing of the chlorine atom with the phosphorus atom, i.e. the share of the third-order reaction of the overall Ad_E process, is greater than that in the reaction with PhSCl. Thus, the addition of dimethoxyphosphorylsulfenyl chloride to *O,O*-diethyl vinylphosphonate, even in a polar solvent (such as C_6H_5CN, CH_3CN), proceeds with participation of the Ad_{E^3} reaction (Table 2).[104,108] Increased steric hindrance of the double bond in the isopropenylphosphonate leads to a situation where the interaction with the *P*-sulfenyl chloride proceeds in an unusual fashion, according to the Ad_{E^3} mechanism.

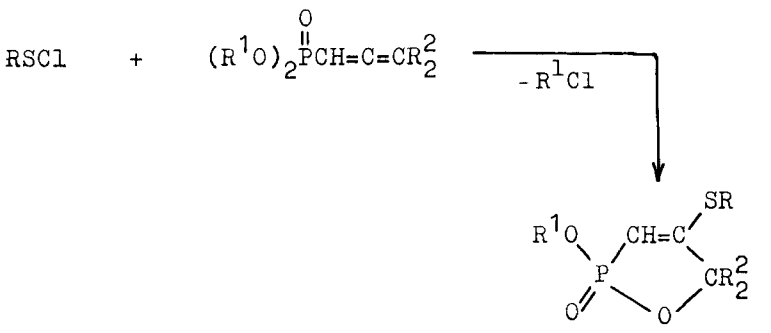
9.2. *With Allenylphosphonates*

The pathway of the reaction of dialkoxyphosphorylsulfenyl chlorides with esters of 3,3-disubstituted allenylphosphonic acids is first of all determined by the presence of a phosphoryl group in an unsaturated compound.[110] The stabilization of the positive charge at the terminal carbon atom of the cumulene which appears as a result of the electrophilic attack on the 2,3-double bond in this case takes place not at the expense of the P=O group of the sulfenyl chloride, but by means of an internal nucleophile in the substrate, i.e. the phosphoryl oxygen. The cyclic quasi-phosphonium intermediate **92** formed in the reaction suffers dealkylation under the action of the chloride anion to form, in high yield, the 4-(dialkoxyphosphorylthio)-1,2-oxaphospholene **93** (Scheme 17).



Scheme 17.

In the corresponding reaction with alkane- and arenesulfenyl chlorides cyclic 4-(organylthio)-1,2-oxaphosphol-3-enes **94** have also bee obtained.[110-112]



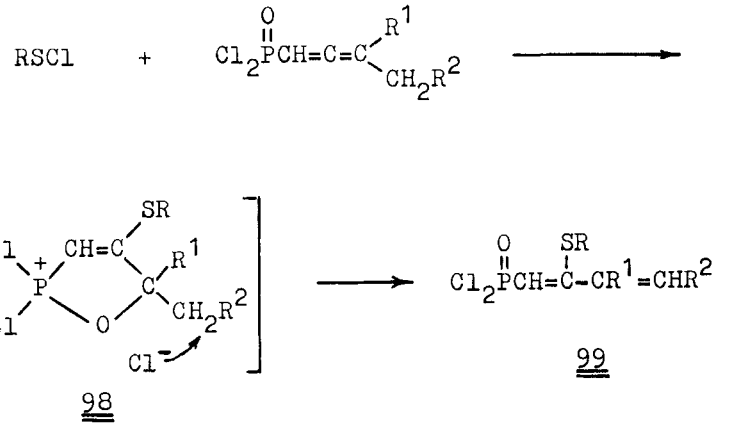
R = alkyl, aryl;

R^1 = alkyl; R^2 = Me; $R_2^2 = (CH_2)_5$

94

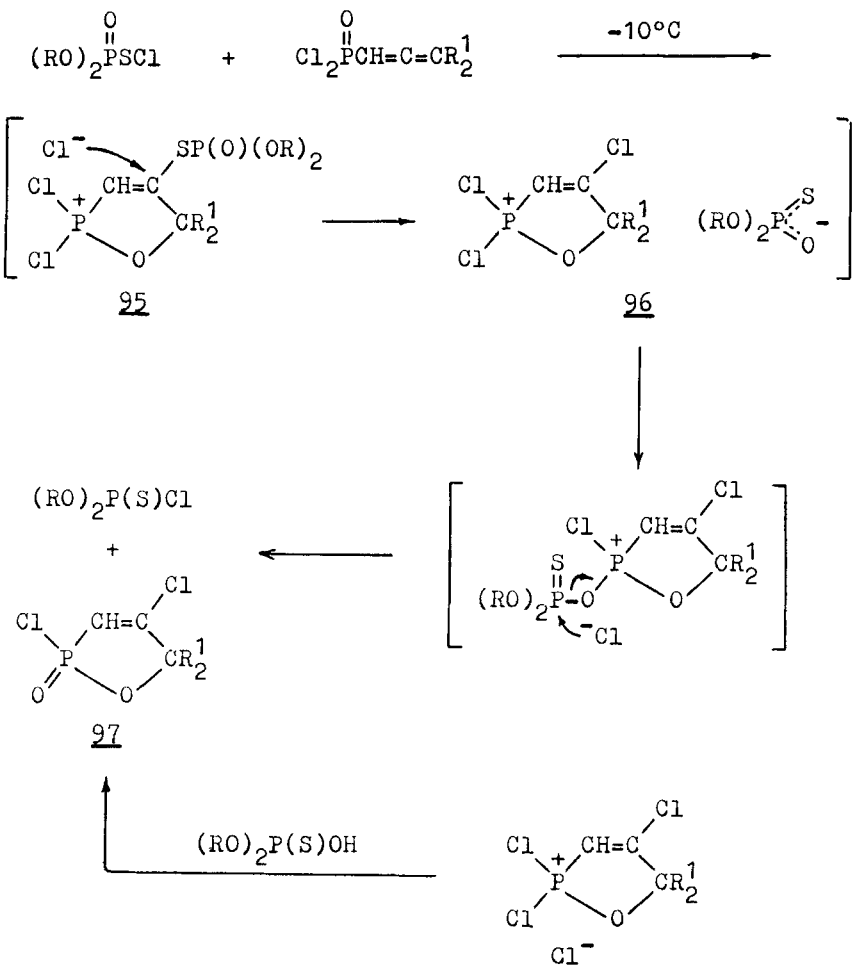
3,3-Disubstituted allenylphosphonic acid dichlorides with dialkoxyphosphorylsulfenyl chlorides evidently form at first 4-(dialkoxyphosphorylthio)-1,2-oxaphospholenium chloride **95**.[113] Further, the substitution of the nucleofugal phosphorylthio group by chlorine takes place together with the elimination of an ambident dialkylthiophosphate anion. The exchange of the chlorine atom at the phosphonium center in intermediate **96** by oxygen results in 2,4-dichloro-2-oxo-1,2-oxa-3-phospholene **97** and a *O,O*-dialkyl chlorothiophosphate (Scheme 18). A compound **97** has also been obtained by an individual synthesis based on 1,2-oxa-3-phospholenium chloride and *O,O*-dialkylthiophosphorous acid.[113]

In the case of organylsulfenyl chlorides 2-(organylthio)butadienyl-1,3-phosphonic acid dichlorides **99** are possibly formed via the 1,2-oxa-3-phospholenium chlorides **98**.[110,112,113]



98 **99**

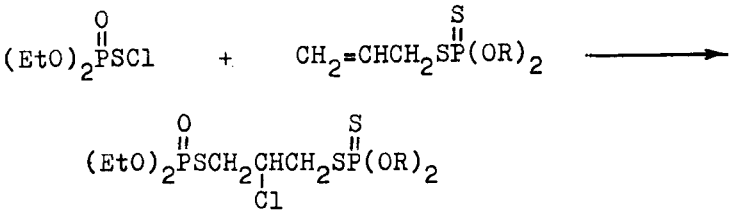
R = alkyl, aryl; R^1 = Me; R^2 = H; $R^1 + R^2 = (CH_2)_4$



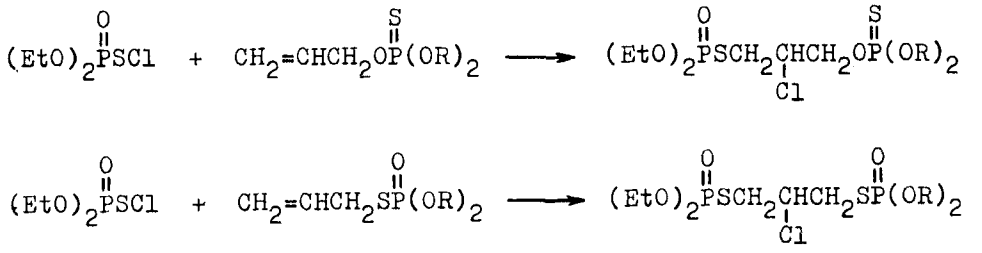
Scheme 18.

9.3. With Allyl thio(dithio)phosphates

Diethoxyphosphorylsulfenyl chloride adds to the double bond of *O,O*-dialkyl *S*-allyl dithiophosphates.[114]

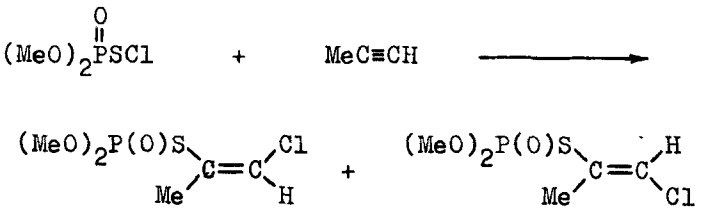


The reaction of diethoxyphosphorylsulfenyl chloride with *O,O*-dialkyl *O*-allyl and *O,O*-dialkyl *S*-allyl thiophosphates[115] proceeds in a similar fashion.

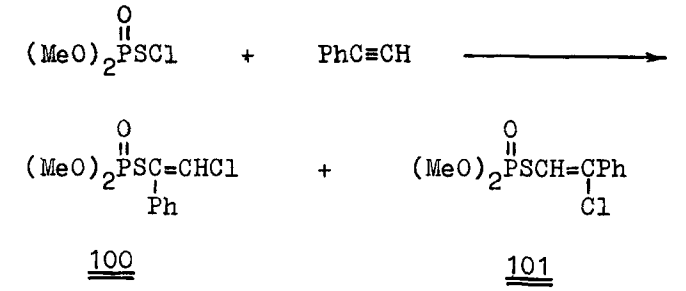


10. REACTIONS WITH ACETYLENE DERIVATIVES

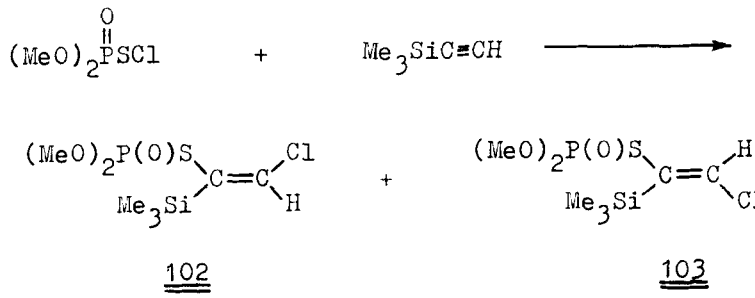
Reactions of *P*-sulfenyl chlorides with alkynes have been considerably less studied than those with alkenes. It has been shown that dimethoxyphosphorylsulfenyl chloride regioselectively adds to propyne, however, the process is not stereoselective.[14]



Upon reaction with phenylacetylene two regioisomeric adducts **100** and **101** with a ratio of 1 : 2 are obtained, each compound being a mixture of *E*- and *Z*-isomers (1 : 1).[17]

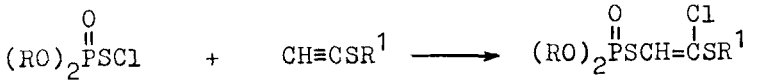


The interaction of dimethoxyphosphorylsulfenyl chloride with trimethylsilylacetylene leads to (*Z*)- and (*E*)-*O,O*-dimethyl *S*-(1-trimethylsilyl-2-chlorovinyl) thiophosphate **102** and **103** in a 3 : 1 ratio and a yield of 97%.[17]

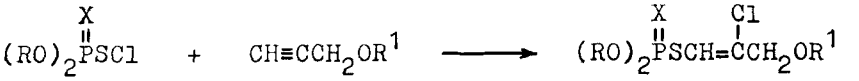


102 103

The reaction of *P*-sulfenyl chlorides with (alkylthio) acetylenes proceeds regioselectively.[16]

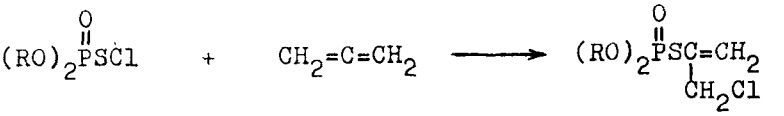


Among the products of the addition of phosphorylsulfenyl chlorides to propargyl alcohol derivatives compounds with high pesticidal activity have been found.[116-118]



R = alkyl; R^1 = alkyl, $Alk_2NC(O)$, AlkOC(O), AlkSC(O); X = O,S

The reaction with allene results in addition of one *P*-sulfenyl chloride molecule.[14]



R = AlkO, Alk

11. SUMMARY

The data presented in this review demonstrate the wide synthetic possibilities of reactions of phosphorus-containing sulfenyl chlorides with unsatured compounds. As a result of these processes various functionally substituted thiolophosphates can be obtained containing saturated or unsaturated organic and elementoorganic groups.

The presence of the electron-withdrawing and considerably bulky phosphoryl group directly bonded to the sulfur atom affects the specific character of the chemical behavior of *P*-sulfenyl chlorides. It is already displayed at the initial stage of the interaction where an activated complex of the π-type is formed in which the relative orientation of the reaction partners is determined by the combined electronic and steric factors. The structure of the intermediate is characterized by considerable electron deficiency at the

unsaturated reaction center in the stabilization of which the electrophilic phosphoryl group participates. These circumstances determine the dependence of the addition regiochemistry not only on the electronic and steric effects of the substituents in the unsaturated reagent, but also on the bulk of the alkoxy groups at the phosphorus atom of the sulfenyl chloride. Due to the lower nucleophilicity of the thiol sulfur atom, the ratio of regioisomers is kinetically and thermodynamically controlled; therefore, *P*-sulfenyl chloride adducts are, as a rule, not subject to regioconversion.

The pronounced carbenium character of the intermediate facilitates in a number of cases (reactions with asymmetric alkenes, unsaturated silicon compounds and organotin compounds) unconventional routes of Ad_E character, accompanied by deprotonation of the intermediate, elimination of silicon- and tin-containing groups, and structural rearrangements. The importance of these routes can be increased in highly polar media (for instance, in the nitromethane-lithium perchlorate system). For the majority of organic electrophiles the intermediate has the structure of an episulfonium ion pair which provides for the preferential formation of adducts. Transformation processes take place only under conditions of increased electrophilicity of the organylsulfenyl chloride. For the phosphoryl group of *P*-sulfenyl chlorides the possibility of direct participation in the final stage of the Ad_E reaction has also been demonstrated: in the reaction with alkenylsilatranes migration of the silatranyl group to phosphoryl oxygen is observed.

All these facts give every reason to consider phosphorus-containing sulfenyl chlorides as useful and promising reagents in organic synthesis which will permit to successfully solve various theoretical and preparative problems of organic and elementoorganic chemistry and to obtain compounds with practical applications.

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