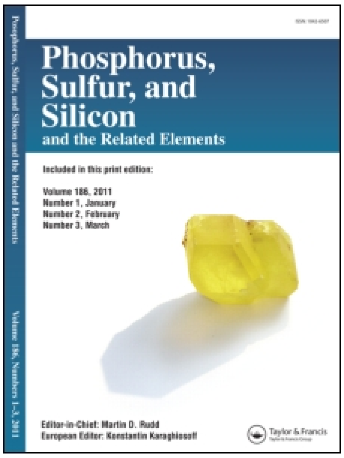

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INTERACTION OF SULFENYL CHLORIDES WITH UNSATURATED ORGANOPHOSPHORUS COMPOUNDS: Ad_E3 REACTION MECHANISM AND REGIOCHEMISTRY OF ADDITION

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INTERACTION OF SULFENYL CHLORIDES WITH UNSATURATED ORGANOPHOSPHORUS COMPOUNDS: Ad_E3 REACTION MECHANISM AND REGIOCHEMISTRY OF ADDITION

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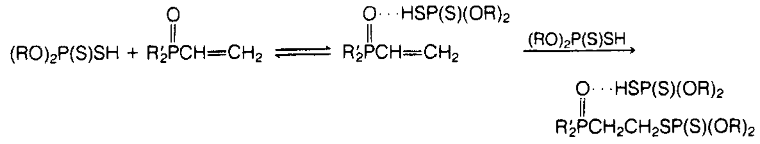
As evidenced by ^1H, ^{31}P, and ^{13}C NMR spectroscopy, phenylsulfenyl chloride, like phosphonosulfenyl chloride,[1] adds to vinylphosphonates to produce a mixture of two regioisomers. Thermodynamic stability of β-chloroadducts is greater than that of α-chloroisomers. The 1,2-addition of C_6H_5SCl to isopropenyl- and styrylphosphonates and unsaturated thionophosphoryl compounds is regiospecific. Kinetic studies have established that the reactions might proceed by the Ad_E3-mechanism involving two molecules of an unsaturated reagent. The substituents at phosphorus and the carbon–carbon double bond in phosphonates affect the structure of the transition state in the limiting stage of the reaction, as does the medium. The effect of the organophosphorus group in the unsaturated reagent and sulfenyl chloride on the mechanism of the Ad_E-process has been analyzed.

INTRODUCTION

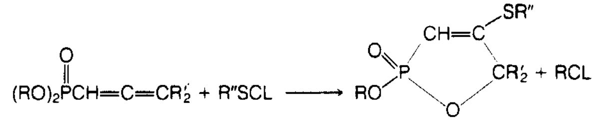
The nucleophilic and electrophilic addition to the unsaturated organophosphorus compounds is a convenient and popular means of introducing functional groups into phosphorus systems.[2–6] As distinct from the Ad_N-processes[7–9] the character of the interaction of the vinyl derivatives of phosphorus with the electrophilic reagents considerably depends on the electron density distribution both in the double bond C=C and within the phosphorus-containing fragment.[10] As compared with the unsaturated phosphonates and thionophosphoryl compounds, dithioacids of phosphorus add to vinylphosphine oxides unexpectedly rapidly. This should be attributed to a strong hydrogen bonding of the acid to the oxygen atom of the phosphoryl group.[11,12] The complexation markedly reduces the activation barrier and affects the kinetics of the process: the addition to vinylphosphine oxides obeys the equation of third order, which is second in dithioacid.



$$(RO)_2P(S)SH + R'_2\overset{\overset{O}{\|}}{P}CH{=}CH_2 \rightleftharpoons R'_2\overset{\overset{O\cdots HSP(S)(OR)_2}{\|}}{P}CH{=}CH_2 \xrightarrow{(RO)_2P(S)SH} R'_2\overset{\overset{O\cdots HSP(S)(OR)_2}{\|}}{P}CH_2CH_2SP(S)(OR)_2$$

The bromination of the unsaturated organophosphorus compounds occurs along similar lines if one goes from vinylphosphonates and phosphinates to vinylphosphine oxides.[13]

The phosphorus-containing group determines the direction of the electrophilic addition. This is clearly seen in the reactions of sulfenyl chlorides with allenylphosphonates. Esters of γ,γ-disubstituted allenylphosphonic acids combine with organylsulfenyl chlorides to produce oxaphospholenes (**1**).[14]



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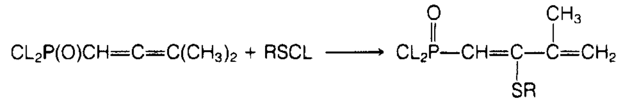
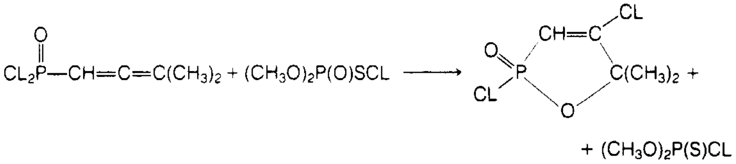
The product of the interaction of dichloroanhydride of γ,γ-dimethylallenylphosphonic acid with RSCl has a diene structure (**2**).[15]



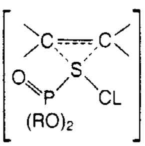
$$CL_2P(O)CH{=}C{=}C(CH_3)_2 + RSCL \longrightarrow CL_2\overset{\overset{O}{\|}}{P}{-}CH{=}\underset{\underset{SR}{|}}{C}{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2$$

2

The phosphorus group, however, directs the reaction by another route.[16]



Kinetic and thermochemical studies of the addition of phenyl- and phosphonosulfenyl chlorides to the unsaturated systems established a considerable dependence of the reaction mechanism on the nature of substituent in the electrophilic reagent.[17,18] The limiting stage of the reaction of phosphorus-containing sulfenyl chlorides with styrene and vinylsilane involves a σ-sulfuran type transition state (**3**); C_6H_5SCl directs the reaction through an activated complex (**4**) similar to the ionic pair.



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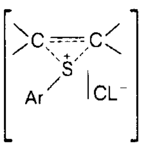

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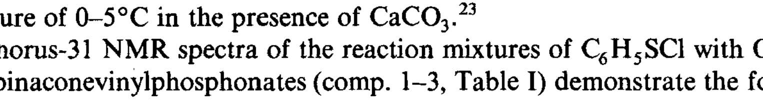
The changes in structure of the transition state are accompanied by corresponding changes the factors controlling the Ad_E-process. The shift of electron density from π-system of the olefin to the sulfur of the electrophile dominates the interaction of phosphonosulfenyl chloride with the unsaturated compounds. Therefore, acceptor substituents in the phosphoryl group accelerate the interaction. With arylsulfenyl chloride, the situation is different: the electron-donating substituents in the aromatic ring promote the polarization of the S—Cl bond in the transition state (4).[19] An alteration of the π-donor properties of olefins produces similar changes in the structure of the activated complex.[19,20]

We have investigated the interaction of phenyl- and phosphonosulfenyl chlorides with the unsaturated organophosphorus compounds in order to elucidate the effect of phosphorus-containing group on the reactivity of the C=C double bond and nature of the products.

RESULTS AND DISCUSSION

Regiochemistry of addition

The data on the addition of organylsulfenyl chlorides to vinylphosphonates available in the literature[21] point to a regiospecificity of the process. They are at contradiction with the formation of two isomers in the reactions of alkyl- and arylsulfenyl chlorides with the derivatives of acrylic acid[22] as well as with the pattern of the interaction between O,O-dimethyl phosphonosulfenyl chloride and O,O-diethyl vinylphosphonate.[1] In the latter case, α-chloro-(5) and β-chloroadducts (6) are thermodynamically stable, and their ratio (1 : 1) is independent of the reaction conditions.



$$(CH_3O)_2P(O)SCL + (C_2H_5O)_2P(O)CH{=}CH_2 \longrightarrow$$

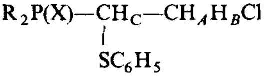
$$(C_2H_5O)_2P(O)\underset{\textstyle CL}{CH}—CH_2SP(O)(OCH_3)_2 + (C_2H_5O)_2P(O)\underset{\textstyle CH_2CL}{CH}—SP(O)(OCH_3)_2$$

5 **6**

Phenylsulfenyl chloride easily adds to vinylphosphonates with exothermic effect. To avoid a possible isomerization of the adducts, the reaction was conducted at a temperature of 0–5°C in the presence of $CaCO_3$.[23]

Phosphorus-31 NMR spectra of the reaction mixtures of C_6H_5SCl with O,O-dialkyl and pinaconevinylphosphonates (comp. 1–3, Table I) demonstrate the formation

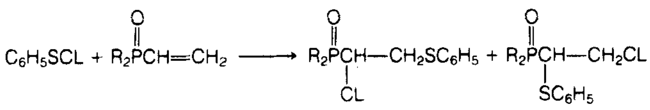
TABLE I



^{1}H and ^{31}P NMR data for $R_2P(X)—\underset{\textstyle SC_6H_5}{CH_C}—CH_AH_BCl$

			δ_H, ppm			J, Hz						δ_P of regioisomers, ppm		
No	R	X	H_A	H_B	H_C	$^2J_{AB}$	$^3J_{BC}$	$^3J_{AC}$	$^3J_{PH_A}$	$^3J_{PH_B}$	$^2J_{PH_C}$	(**8**)	(**7**)	(**8**)/(**7**)* %
1	CD_3O	O	3.86	3.54	3.29	−11.5	8.5	4.5	11.5	8.0	−18.0	23.1	20.3	90/10
2	i-C_3H_7O	O	3.92	3.45	3.10	−11.5	9.5	4.0	9.0	6.0	−18.5	17.2	13.4	70/30
3		O	3.88	3.60	3.15	−11.5	8.5	5.5	10.0	14.0	−14.5	32.0	30.1	80/20
4	Cl	O	4.20	3.73	3.88	−11.0	9.5	2.5	11.0	6.0	−17.0	46.4	—	100/0
5	i-C_3H_7O	S	4.21	3.72	3.45	−11.5	9.5	3.7	10.0	7.5	−16.0	84.3	—	100/0

*(**8**)/(**7**) at R = C_2H_5 and X = O 80/20; R = $ClCH_2CH_2$ and X = O 95/5.



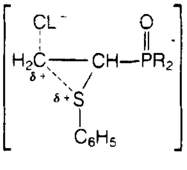
$$C_6H_5SCL + R_2\overset{O}{\overset{\|}{P}}CH{=}CH_2 \longrightarrow R_2\overset{O}{\overset{\|}{P}}\underset{CL}{\underset{|}{C}}H{-}CH_2SC_6H_5 + R_2\overset{O}{\overset{\|}{P}}\underset{SC_6H_5}{\underset{|}{C}}H{-}CH_2CL$$

7 **8**

of two regioisomers (**7**, **8**) in the electrophilic addition. The initial ratio of peak intensities changes with time in favour of a thermodynamically more stable β-chloroadduct.

The structure of (**8**) was proved by ^1H NMR spectroscopy. The methylene and methyne protons form with phosphorus a four-spin $ABCX$-system which by phosphorus decoupling transforms into ABC-system. As follows from Table I, H_A and H_B resonate downfield from H_C, which should be attributed to the electron-accepting effect of chlorine. In the spectrum of isomer (**7**) the methylene and methyne resonances bands have to be reversed.[24] Comparing the spectra of O, O-diisopropyl 1,2-dichloroethylphosphonate[25] and O,O-diisopropyl 2-chloro-1-phenylthioethylphosphonate, we see that the difference in the methyne chemical shifts ($\Delta\delta_{H_C} = 0.92$ ppm) considerably exceeds that of the methylene protons ($\Delta\delta_{H_A,H_B} \sim 0.25$ ppm). The geminal coupling constant $^2J_{AB}$ varies only slightly (from -11.0 to -11.5 Hz), as illustrated in Table I, and corresponds to $^2J_{HH}$ for the CH_2Cl-fragment in the aliphatic series.[24,26] This is another proof of the formation of β-chloroadducts in the reaction of phenylsulfenyl chloride with vinylphosphonates. The additional multiplets in the region of 3.2–3.9 ppm are indicative of the formation of the second regioisomer. The signals of A, B, and C protons overlap the low-intensity resonances of α-chloroadducts, preventing the assignment of the $A'B'C'X$-system for (**7**).

As the electron-withdrawing properties of the phosphorus-containing group are enhanced the fraction of β-chloroadduct increases and with dichloroanhydride of vinylphosphonic acid it becomes the sole product of the reaction. The reason of such a relationship is connected probably with destabilization by phosphorus substituent of the partial positive charge at α-carbon in the transition state (**9**) in the second product-determining stage of the electrophilic addition. This results in that the chlorine anion opens the episulfonium cycle at the terminal carbon.



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The figure shows the ABC-part of the ^1H NMR spectrum of O,O-dimethyl 2-chloro-1-phenylthioethylphosphonate-D_6.[27] Vicinal coupling constants ($^3J_{AC}$ 4.5 Hz, $^3J_{BC}$ 8.5 Hz) give by the Karplus correlation for $^3J_{HH}$ (which does not take into account the electronegativities and orientation of substituents in the ethane fragment[28]) the skewed conformation (**10**) with the following dihedral angles $\angle H_ACH_C \sim 50°$ and $\angle H_BCH_C \sim 135°$. It follows that the C_6H_5S-group and chlorine occupy in the Newman projection trans-positions relative to the carbon–carbon bond, which

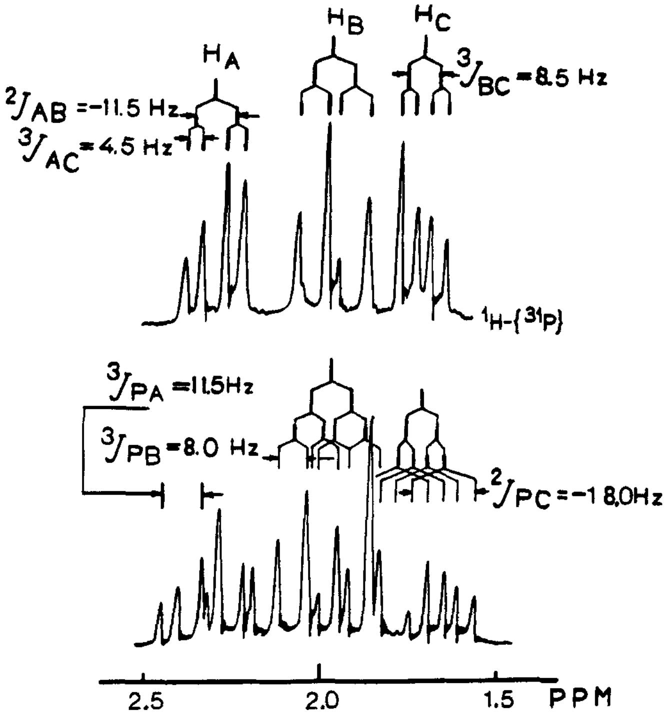
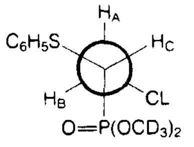


FIGURE 1 ^1H and $^1H\text{-}\{^{31}P\}$ NMR spectra of $(CD_3O)_2P(O)\underset{SC_6H_5}{\underset{|}{CH_C}}-CH_ACH_BCl$.

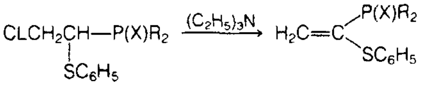
accords with the stereospecificity of the trans-addition of sulfenyl chlorides to the unsaturated systems.[29]

The analysis of carbon-13 NMR spectra of the phenylsulfenyl chloride-vinylphosphonate adducts (**8**) shows that the terminal carbon resonates upfield from the methyne carbon (comp. 1–5. Table II). With enhancing electron-accepting properties of substituents at phosphorus, the difference between δ_{C_1} and δ_{C_2} increases to 19.3 ppm, and $^1J_{C_1P}$ decreases to 97.0 Hz. The validity of the chemical shift assignments has been confirmed by the off-resonance experiment.



10

Vacuum distillation of the addition products of phenylsulfenyl chloride to esters of vinylphosphonic acid results in their partial dehydrochlorination. Treating the reaction mixtures with triethylamine in ether produces the unsaturated phosphonates (**11**); their structure has been supported by spectral data.

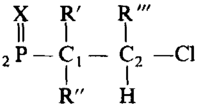


8 **11**

X=O,S;R=ALKO,CL.

The PMR spectra of these compounds visualize two characteristic doublets in the region of olefin proton chemical shifts (Table III). The absence of spin–spin coupling between protons *A* and *B* is indicative of their geminal location; the angle C–H_A and C–H_B probably approaches 120°.[30] As follows from Table III, the replacement of the alkoxyl groups at the phosphorus atom by chlorine considerably increases the vicinal constants $^3J_{PH}$. This points to the enhancement of the s-character of the P—C bond in the fragment P—C=C—H.

TABLE II

^{13}C NMR data for

$R_2\overset{\overset{X}{\|}}{P}-\underset{R''}{\overset{R'}{C_1}}-\underset{H}{\overset{R'''}{C_2}}-Cl$

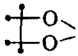
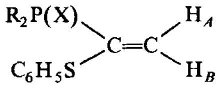
No	R	R′	R″	R‴	X	$\delta_{^{13}C}$, ppm				*J*, Hz	
						C_1	C_2	R	CH_3	$^1J_{C_1P}$	$^2J_{C_2P}$
1	CH_3O	H	SC_6H_5	H	O	48.0	43.3	53.5	—	145.6	−4.4
2	i-C_3H_7O	H	SC_6H_5	H	O	47.11	41.36	21.72 69.45	—	145.6	−5.9
3	i-C_3H_7O	H	SC_6H_5	H	S	49.25	43.9	23.86 72.2	—	145.6	−5.9
4		H	SC_6H_5	H	O	47.4	40.8	—	—	135.3	−4.4
5	Cl	H	SC_6H_5	H	O	61.3	42.0	—	—	97.0	−13.24
6	CH_3O	SC_6H_5	CH_3	H	O	50.85	48.84	53.55	19.7	131.3	−10.3
7	i-C_3H_7O	SC_6H_5	CH_3	H	O	49.5	49.3	23.87 71.0	19.63	148.5	−10.24
8	Cl	SC_6H_5	CH_3	H	O	61.2	47.12	—	19.5	95.6	−22.06
9	i-C_3H_7O	Cl	CH_3	H	O	63.53	51.9	23.7 72.2	24.24	155.9	−9.4
10	i-C_3H_7O	H	SC_6H_5	C_6H_5	O	56.8	61.0	23.64 71.63	—	145.6	−8.83

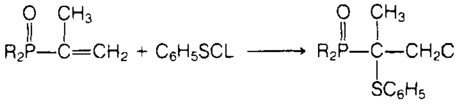
TABLE III

^{1}H and ^{31}P NMR data for

$R_2P(X)(C_6H_5S)C{=}CH_AH_B$

R	X	δ_H, ppm			*J*, Hz		δ_P, ppm
		H_A	H_B	R	$^3J_{PH_A}$	$^3J_{PH_B}$	
CH_3O	O	6.20	5.51	3.73	19.0	42.0	17.3
i-C_3H_7	O	6.13	5.30	1.24 4.59	20.0	42.0	17.2
Cl	O	6.53	5.80	—	25.0	58.0	31.0
i-C_3H_7O	S	6.27	5.34	1.25 4.73	22.0	47.0	79.5
Cl	S	6.75	5.76	—	28.0	63.0	82.2

Thus, the addition of phenylsulfenyl chloride to vinylphosphonates proceeds predominantly or exclusively (depending on the nature of substituents at the phosphorus atom) with the formation of 2-chloro-1-phenylthioethylphosphonates (**8**). The regioisomers (**7**) are thermodynamically less stable than β-chloroadducts.

Contrary to vinylphosphonates, the isopropenyl analogues (**12**) react with C_6H_5SCl to produce the sole isomer (**13**).



$$R_2\overset{\overset{\displaystyle O}{\|}}{P}-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 + C_6H_5SCL \longrightarrow R_2\overset{\overset{\displaystyle O}{\|}}{P}-\underset{\underset{\displaystyle SC_6H_5}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2CL$$

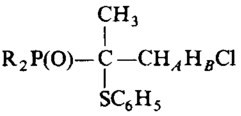
12 **13**

Chemical shifts of the phosphonate (**13**) methylene protons (Table IV) are close to δH_A and δH_B of the corresponding β-chloroadducts (**8**) which confirms β-orientation of the chlorine in addition to isopropenylphosphonates. The predominant formation of the anti-Markovnikoff product was also noted in the reactions of sulfenyl chlorides with the derivatives of methacrylic acid.[24] Carbon-13 NMR spectra data (Table II) support the proposed structure of the adducts (**13**). The comparison of the chemical shifts of α- and β-carbons in O,O-diisopropyl 2-chloro-1-phenylthioisopropylphosphonate and model O,O-diisopropyl 1,2-dichloroisopropylphosphonate (comp. 7, 9, Table II) shows that only α-carbon chemical shift changes considerably ($\Delta\delta_{C_1} = 14$ ppm), whereas the corresponding difference for the methylene carbon is small ($\Delta\delta_{C_2} = 2.6$ ppm). Therefore it may be concluded that C_6H_5S-group in the adduct occupies α-position with respect to the phosphorus-containing substituent. The introduction of chlorine into the phosphorus fragment also increases significantly δ_{C_1} (comp. 8, Table II).

The regiospecificity of C_6H_5SCl addition to isopropenylphosphonates (**12**) should apparently be attributed to the methyl and phosphorus groups sterically impeding the chlorine-anion attack on α-carbon in the cyclic imtermediate.

In styrenephosphonates (**14**), the phenyl group at the double bond stabilizes the partial positive charge at the adjacent carbon. This combined with the orientation effect of the phosphorus substituent leads to the formation of adducts (**15**).

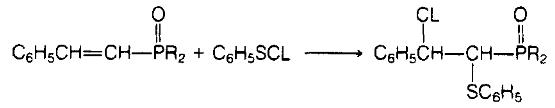
TABLE IV



^1H and ^{31}P NMR data for $R_2P(O)-\underset{\underset{\displaystyle SC_6H_5}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_AH_BCl$

R	δ_H, ppm			J, ppm				δ_P, ppm
	H_A	H_B	CH_3	$^2J_{AB}$	$^3J_{PH_A}$	$^3J_{PH_B}$	$^3J_{PCCH_3}$	
CH_3O	3.55	—*	1.29	−12.0	8.1	—	15.0	28.2
i-C_3H_7O	3.49	3.73	1.25	−12.0	9.0	6.70	15.0	19.4
Cl	3.68	3.90	1.48	−12.0	10.1	7.86	25.0	51.3

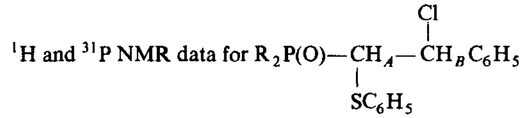
*H_B resonates in the chemical shift region of OCH_3-group.



14 **15**

Hydrogen-1 NMR spectra of these compounds (Table V) demonstrate that chemical shifts of *A* and *B* protons are close to δ_H of β-chloroadducts of phenylsulfenyl chloride with the derivatives of cinnamic acid (δ_{H_A} ~ 4.2 ppm; δ_{H_B} ~ 5.4 ppm) and differ considerably from the analogous parameters of α-chloroisomers (δ_{H_B} ~ 4.8 ppm).[22] Vicinal constants $^3J_{AB}$ and $^3J_{PH_B}$ are probably virtual since in all compounds $^3J_{AB} = {}^3J_{PH_B}$.

TABLE V



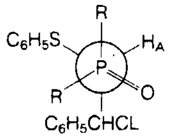
^{1}H and ^{31}P NMR data for $R_2P(O)—\underset{SC_6H_5}{CH_A}—\overset{Cl}{CH_B}C_6H_5$

	δ_H, ppm		J, Hz			
R	H_A	H_B	$^3J_{AB}$	$^2J_{PH_A}$	$^3J_{PH_B}$	δ_P, ppm
CH_3O	3.81	5.57	6.0	−20.0	6.0	22.0
i-C_3H_7O	3.56	5.56	4.5	−20.5	4.5	18.1
Cl	4.20	5.81	4.0	−16.5	4.0	43.9

Certain evidence on the conformation of phosphonates (**15**) relative to the P—C bond gives the geminal constant $^2J_{P^{IV}CH}$. By the graph depicting the dependence between $^2J_{PH}$ and the orientation of the P=O bond to the plane of three atoms P^{IV}, C, and H, the geminal constants for the phosphonate surroundings should be equal to −14 to −16 Hz.[31] These are the averaged values owing to a quick exchange between one trans- and two gauche-conformations. The heteroatom in the P(O)—CH fragment decreases $^2J_{PH}$ (the absolute value rises) at angles of 0–70° and increases at 80–180°. In adducts (**15**), $^2J_{PH_A}$ is equal to −16.5 to −20 Hz (Table V). This probably points to the predominant skewed conformation (**16**), wherein the axis of the P=O bond forms with the PCH_A plane an angle of 80°.

Phenylsulfenyl chloride reacts with styrenethiophosphonate in a much more complex manner than with the oxygen analogues; in the former case both the double C=C bond and the P=S group participate in the reaction.[32]

Thus, the investigation of the structure of the products of phenylsulfenyl chloride addition to the unsaturated organophosphorus compounds has demonstrated that,



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contrary to the corresponding derivatives of acrylic acid, the phosphono group promotes predominant or exclusive β-orientation of the chlorine in the product-determining stage of the Ad_E-process. This should apparently be explained first by that the phosphonates sterically impede the reactivity of α-carbon and second by that the phosphorus and carbonyl substituents differently affect the episulfonium cycle.[23,24]

Kinetics and Mechanism of the Reaction

As noted above, the organophosphorus group substituted for the phenyl group in sulfenyl chloride changes the structure of the transition state (**3**,**4**) and hence the factors that control the rate-determining stage of the Ad_E-process. To this end, the effect of the phosphorus-bearing substituent on the mechanism of the electrophilic addition of sulfenyl chlorides is of particular interest.

The spectrophotometric analysis of the interaction of C_6H_5SCl with excess O,O-dialkyl vinylphosphonates revealed a considerable solvent dependence of the addition. With decreasing the solvating properties of the medium, the order of the reaction in vinylphosphonate changes from first to second; whereas that in phenylsulfenyl chloride remains first. The rate law of the reactions has the general form:

$$v = k_2[\mathrm{VP}][\mathrm{SC}] + k_3^{\mathrm{eff}}[\mathrm{VP}]^2[\mathrm{SC}], \tag{1}$$

where [VP], [SC] are the instantaneous concentrations of vinylphosphonate and sulfenyl chloride; k_2 and k_3^{eff} are the rate constants of second and third (effective value) order reactions.

If displayed graphically, the dependence of the observed rate constant of the pseudofirst order on the vinylphosphonate concentration

$$\frac{k_{\mathrm{obs}}}{[\mathrm{VP}]} = k_2 + k_3^{\mathrm{eff}} \cdot [\mathrm{VP}] \tag{2}$$

gives k_2 and k_3^{eff}. They are summarized in Table VI.

TABLE VI

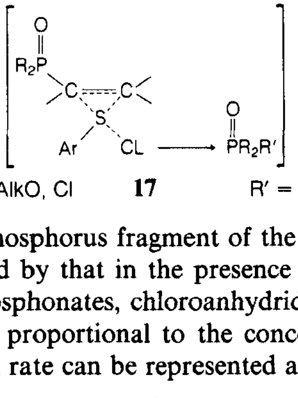
Effect of solvent on the rate constants of reactions between $(RO)_2P(O)CH{=}CH_2$ and C_6H_5SCl at 25°C

	R = C_2H_5		R = $ClCH_2CH_2$	
Solvent	$k_2 \cdot 10^3$, L/(mol · s)	$k_3^{\mathrm{eff}} \cdot 10^3$, $L^2/(mol^2 \cdot s)$	$k_2 \cdot 10^3$, L/(mol · s)	$k_3^{\mathrm{eff}} \cdot 10^3$, $L^2/(mol^2 \cdot s)$
Tetrachloromethane*	0.03	0.68	—	0.57
Benzene	0.29	1.15	—	0.72
Chlorobenzene	1.52	2.10	0.14	1.46
1,4-Dioxane	3.10	2.60		
1,2-Dichloroethane	12.7	—	3.74	—
Benzonitrile	20.2	—		
Acetonitrile	49.6	—	27.6	—

*For R = CH_3, $k_3^{\mathrm{eff}} = 0.48 \cdot 10^{-3} L^2/(mol^2 \cdot s)$.

In nonpolar weakly solvating media, where the interaction proceeds slowly, the overall order of the Ad_E-process is third or intermediate between second and third. When the reaction is conducted in more polar solvents the bimolecular flow becomes predominant. The contribution of the Ad_E 2-interaction of O,O-diethyl vinylphosphonate with C_6H_5SCl in the overall chemical process at [VP] = 0.3 mol/L accounts for: CCl_4 13%, C_6H_6 46%, C_6H_5Cl 71%, $ClCH_2CH_2Cl$ 100%.

The additional stabilization of the transition state (**17**) in the limiting stage of the reaction through the coordination of sulfur of sulfenyl chloride and phosphorus of the unsaturated partner requires in weakly solvating media a second molecule of the phosphorus reagent. Such a complexation enhances the polarity of the S—Cl bond and thus increases the electrophilicity of sulfur. This promotes a further shift of the electron density from the π-system of vinylphosphonate to the electrophilic centre. The process is especially important for the unsaturated phosphorus compounds, the ionization potentials of which are sufficiently high (10.6–11.5 eV).[33] The decrease in the π-donor properties of the double bond C=C makes the reaction of the electrophilic addition of C_6H_5SCl to O,O-dimethyl and O,O-di(2-chloroethyl) vinylphosphonates obey exclusively the rate law of third order in media (CCl_4, C_6H_6), where the interaction of more donor O,O-diethyl vinylphosphonate involves also the bimolecular flow (Table VI).



R = AlkO, Cl **17** R′ = AlkO, Cl, $CH_2 = CH$

The participation of the phosphorus fragment of the unsaturated phosphonate in the coordination is confirmed by that in the presence of the saturated phosphoryl compounds (phosphates, phosphonates, chloroanhydrides of phosphorus acids) the rate of C_6H_5SCl addition is proportional to the concentration of the phosphorus additive. The overall reaction rate can be represented as

$$v = k_2[\mathrm{VP}] \cdot [\mathrm{SC}] + k_3^{\mathrm{eff}}[\mathrm{VP}]^2[\mathrm{SC}] + (k_3^{\mathrm{eff}})'[\mathrm{VP}][\mathrm{SC}][\mathrm{P}], \qquad (3)$$

where $(k_3^{\mathrm{eff}})'$ is the effective rate constant of third order reaction with the participation of a saturated phosphorus compound; [P] is the concentration of a phosphorus additive.

A saturated phosphonate activates the Ad_E-process because of the contribution of the new third order reaction flow where the role of n-acceptor performs not the second molecule of vinylphosphonate but rather the saturated phosphoryl compound. The partial rate constants for the reaction of O,O-diethyl vinylphosphonate and phenylsulfenyl chloride in the presence of triethyl phosphate were found to be as follows: $k_2 = 0.49 \cdot 10^{-3}$ L/mol · s; $k_3^{\mathrm{eff}} = 2.1 \cdot 10^{-3}$ L^2/mol^2 · s; $(k_3^{\mathrm{eff}})' = 2.44 \cdot 10^{-3}$ L^2/mol^2 · s. In the absence of triethyl phosphate: $k_2 = 0.55 \cdot 10^{-3}$ L/mol · s and $k_3^{\mathrm{eff}} = 1.95 \cdot 10^{-3}$ L^2/mol^2 · s. The values of k_3^{eff} and $(k_3^{\mathrm{eff}})'$ are close, which stems from the similarity of the structure of the unsaturated reagent and saturated phosphorus compound. The third component practically does not affect k_2 and k_3^{eff}.

This suggests that the main solvation characteristics of the medium remain invariable and confirms the *n*-acceptor role the phosphate plays in the interaction. With growing concentrations of the saturated phosphoryl reagent, the fraction of the catalyzed Ad_E-process increases, and the reaction order in vinylphosphonate approaches unity. The substituents at phosphorus practically have no effect on the catalytic activity of the phosphorus additive: $Cl_2P(O)CH_3$ $(k_3^{eff})' = 2.46 \cdot 10^{-3}$ $L^2/mol^2 \cdot s$; $(C_2H_5O)_2P(O)CH_3$ $(k_3^{eff})' = 3.23 \cdot 10^{-3}$ $L^2/mol^2 \cdot s$.

In polar strongly solvating media, the transition state is sufficiently stabilized by solvent molecules, and the participation of a phosphorus-containing reagent is not necessary. Therefore the reaction is bimolecular.

The linear dependence

$$\log k_3^{eff} = -(1.86 \pm 0.06) + (0.29 \pm 0.02)\log k_2 \qquad R = 0.994, \quad S_0 = 0.029, \quad n = 4 \tag{4}$$

shows that the interaction between O,O-diethyl vinylphosphonate and phenylsulfenyl chloride in different solvents obeys in general the rate laws of second and third orders. A small proportionality factor suggests that the Ad_E3-process is considerably less sensitive to the change in the medium than the bimolecular interaction. This should apparently be attributed to the coordination and shielding of the nucleophilic and electrophilic centres in the activated complex (**17**) by the second vinylphosphonate molecule.

The solvation of the transition state of the second order reaction between C_6H_5SCl and diethyl vinylphosphonate is affected greatly by properties of the solvent such as, say, polarity, polarizability and some specific influence of the medium.

$$\log k_2 = (-10.2 \pm 1.13) + (7.52 \pm 0.53)Y + (10.98 \pm 3.11)P + (0.308 \pm 0.064)E + (0.0039 \pm 0.0009)B \qquad R = 0.997, \quad S = 0.150, \quad n = 7. \tag{5}$$

Here, $Y = (\varepsilon - 1)/(2\varepsilon + 1)$, $P = (n^2 - 1)/(n^2 + 1)$, E = solvent electrophilic index, B = solvent nucleophilic index.

The reaction of C_6H_5SCl with styrene[18] yields the similar dependence

$$\log k_2 = (-11.2 \pm 1.88) + (11.626 \pm 1.686)Y + (16.816 \pm 4.988)P + (0.624 \pm 0.106)E \qquad R = 0.987, \quad S_0 = 0.435, \quad n = 8. \tag{6}$$

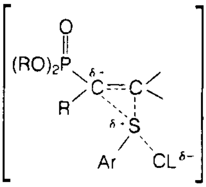
The comparison of eqs. (5) and (6) shows that when organophosphorus group is substituted for phenyl in an unsaturated reagent, the addition markedly decelerates and the reaction becomes less sensitive to the solvent. The reason must be that the Ad_E2-reaction involving vinylphosphonates proceeds through a less polarized intermediate than that involving styrene. This calls for an additional *n*-acceptor when the reactions take place in weak solvating media.

The effect of substituents at phosphorus on the reaction of C_6H_5SCl and vinylphosphonates in acetonitrile is described by eq. (7), due to Kabachnik,[34] the sign of ρ in which is another proof of an electrophilic mechanism (comp. 1–5, Table

VII). A correlation succeeded with σ^{Φ} constants invoked indicates the substituents exert their electronic effect both inductively and mesomerically.[35,36]

$$\log k_2 = -(1.60 \pm 0.01) - (0.76 \pm 0.01)\Sigma\sigma^{\Phi} \qquad (7)$$
$$R = 0.998, \quad S_0 = 0.06, \quad n = 5.$$

Alkyl substituents at the double bond C=C, as a rule, accelerate the interaction of sulfenyl chlorides with olefins.[37-40] With unsaturated organophosphorus compounds, the situation is more complex. Esters of isopropenylphosphonic acid react with arylsulfenyl chlorides in CH_3CN (Ad_E2-mechanism) more eagerly than dialkylvinylphosphonates. However, the ratio of reactivities of the corresponding dichloroanhydrides is reverse: the α-methyl group in isopropenyldichlorophosphonate impedes the process (Table VIII). This may be explained as follows. Sterically loaded α-carbon in phosphonic esters and partial stabilization of excessive positive charge it bears owing to $^{+}$M-effect that the alkoxyl substituents at phosphorus produce (the correlation invoking σ^{Φ}-constants, eq. (7)) favour the asymmetric structure of the transition state (**18**). Chlorines substituted for RO-groups enhance the electron-withdrawing properties of the phosphorus-containing groups and symmetrize the cyclic structure of the transition state. This increases steric hindrance within the activated complex (**19**).[41]



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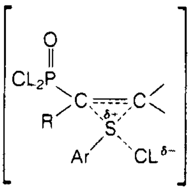

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A greater positive charge localized at the sulfur of the electrophile in the structure (**19**) makes the interaction of unsaturated anhydrides of phosphorus acids with arylsulfenyl chlorides more sensitive to the electron-donating effect of methyl in the aromatic ring than that of phosphonates (Table VIII).[19]

Similar change in the geometry of the transition state of the Ad_E2-reaction of vinyl- and isopropenylphosphonates produces the medium. In acetonitrile, the reactivity of O,O-dimethyl isopropenylphosphonate is greater than that of the corresponding vinyl derivative. The ratio of rate constants of bimolecular interactions k_2 in benzene is reverse (Table VIII). Thus, vital to the stabilization of the asymmetric structure of the transition state (**18**) are both the electron-donating properties of substituents at phosphorus and solvating power of the medium. As a result of the symmetrization of the activated complex (**18** → **19**), $k_2^{CH_3}/k_2^{H}$ for the reactions between unsaturated phosphonates and tolyl- and phenylsulfenyl chlorides carried out in benzene is greater than that for the reactions conducted in acetonitrile (Table VIII).

Sulfenyl chloride adds to styrylphosphonates at a considerably lower rate than to vinylphosphonates. The reason for this might be π-donor properties of C=C bond decreased through the conjugation with the phenyl (Table VII). What is more, styrylphosphonates to a greater degree hinder sterically the Ad_E2-process.

TABLE VII

Effect of substituents on the rate constants of reactions between $R_2P(O)CR' = CHR''$ and C_6H_5SCl (CH_3CN, $t = 25°C$)

No	R	R′	R″	$k_2 \cdot 10^3$ L/(mol · s)
1	Cl	H	H	0.952
2	$ClCH_2CH_2O$	H	H	27.6
3	CH_3O	H	H	34.0
4	C_2H_5O	H	H	49.6
5	i-C_3H_7O*	H	H	67.7
6	Cl	CH_3	H	0.754
7	CH_3O	CH_3	H	50.4
8	i-C_3H_7O	CH_3	H	106.0
9	Cl	H	C_6H_5	0.10
10	i-C_3H_7O	H	C_6H_5	15.0

*$(i\text{-}C_3H_7O)_2P(S)CH{=}CH_2$ in CH_3CN $k_2 = 150 \cdot 10^{-3}$ L/(mol · s): in CCl_4 $k_2 = 0.12 \cdot 10^{-3}$ L/(mol · s) and $k_3^{\text{eff}} = 0.3 \cdot 10^{-2}$ $L^2/(mol^2 \cdot s)$.

The thionephosphoryl group substituted for the phosphoryl enhances the reactivity of vinylphosphonates combining with C_6H_5SCl (Table VII). This may be explained by that phosphorus-containing substituents produce different electronic effects;[42,43] moreover, the specific influence of the sulfur of the P=S group should not be totally excluded.[32]

Phosphonosulfenyl chlorides, as has been shown on the example of their interaction with styrene and vinylsilanes,[17,18] form in the limiting stage of addition a transition σ-sulfuran type complex (3) preserving the S—Cl bond. This gives us grounds to suggest that in phosphonosulfenyl chlorides reacting with vinylphosphonates, the contribution of coordinated chlorine and phosphorus of the unsaturated reagent to the stabilization of the activated complex, i.e. the contribution of third order reaction to the overall Ad_E-process, is greater than in phenylsulfenyl chlorides. Indeed, the addition of O,O-dimethylphosphonosulfenyl chloride to O,O-diethyl vinylphosphonate even in the strongly solvating medium (benzonitrile) is in part third order, second in vinylphosphonate (Table IX). In acetonitrile the reaction is second order. Sterically loaded C=C double bond in isopro-

TABLE VIII

Rate constants of $X_2P(O)CR{=}CH_2$ reaction with C_6H_5SCl (k_2^{H}) and p-$CH_3C_6H_4SCl$ ($k_2^{CH_3}$), $t = 25°C$

X	R	Solvent	$k_2^{H} \cdot 10^3$, L/(mol · s)	$k_2^{CH_3} \cdot 10^3$, L/(mol · s)	$k_2^{CH_3}/k_2^{H}$
Cl	H	CH_3CN	0.95	1.69	1.78
CH_3O	H	CH_3CN	34.0	39.9	1.17
Cl	CH_3	CH_3CN	0.75	1.12	1.49
CH_3O	CH_3	CH_3CN	50.4	48.3	0.96
CH_3O	H	C_6H_6	0.15	0.25	1.67
CH_3O	CH_3	C_6H_6	0.08	0.15	1.87

TABLE IX

Rate constants of $(CH_3O)_2P(O)SCl$ reaction with $(RO)_2P(O)CR' = CH_2$, $t = 25°C$

R	R′	Solvent	$k_2 \cdot 10^3$ L/(mol · s)	$k_3 \cdot 10^3$ $L^2/(mol^2 \cdot s)$
C_2H_5	H	CH_3CN	2.1	—
C_2H_5	H	$ClCH_2CH_2Cl$	1.0	1.2
CH_3	H	CH_3CN	1.3	—
CH_3	CH_3	CH_3CN	—	0.56

penylphosphonate makes the process even in CH_3CN proceed exclusively by third order rate law.

Thus, we have demonstrated that the addition of sulfenyl chlorides to olefins may proceed by the Ad_E3-mechanism with two molecules of unsaturated reagent taking place in transition state formation at limiting stage. The Ad_E3-reaction takes place when the double bond of olefin displays weak π-donating properties and the system has an *n*-acceptor. Vinylphosphonates conveniently combine these properties. In vinylsilanes, silicon promotes the Ad_E-reaction with sulfenyl chlorides to a lesser extent, and its electrophilic contribution does not markedly affect the kinetics of the process.[18]

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Varian HA-100 D spectrometer operating at 100 MHz with TMS as an internal standard. Samples were run as solutions in CCl_4. The analysis of *ABC*-system spectra was carried out by the NMRCAL program on a BNC-12 minicomputer. The ^{31}P NMR spectra were taken on a home made YaMR-KGU-4 spectrometer (10.2 MHz), chemical shifts were referenced to 85% H_3PO_4. The ^{13}C NMR spectra were recorded on a Bruker WH-90 instrument (22.63 MHz).

Vinyl-,[44,45] isopropenyl-,[46] styrylphosphonates,[47] and their thioanalogues were synthesized by the known methods. Reagent purity was checked by GLC. Phenylsulfenyl chloride was prepared from thiophenol as reported in Ref. 51. O,O-Dimethyl phosphonosulfenyl chloride was obtained by the chlorination of trimethyl thiophosphate.[23]

Reaction of phenylsulfenyl chloride with vinylphosphonates. Phenylsulfenyl chloride (0.01 mol) in 10 mL abs. ether was added to the equimolar amount of vinylphosphonate in 5–10 mL ether at 0–5°C in the presence of 0.01–0.02 g $CaCO_3$. The mixture was maintained at this temperature till the colour of the initial sulfenyl chloride faded out. The pale-yellow solution was concentrated in vacuum. Vacuum distillation of the adducts results in their partial dehydrochlorination. Only with dichlorovinylphosphonate and vinylthiophosphonates as the starting compounds, the reaction products were distilled without the decomposition.

Dichloroanhydride of 2-chloro-1-phenylthioethylphosphonic acid: b.p. 108–110°C/0.1 mm. d_4^{20} 1.4642, n_D^{20} 1.6048, δ_P 46 ppm. Found, %: C, 33.13; H, 2.90; P, 10.95. $C_8H_8Cl_3OPS$. Calcd., %: C, 33.19; H, 2.78; P, 10.70.

O,O-Diisopropyl 2-chloro-1-phenylthioethylthiophosphonate: b.p. 115–116°C/0.1 mm, d_4^{20} 1.1860, n_D^{20} 1.5592, δ_P 84 ppm. Found, %: C, 47.66; H, 6.37; P. 8.29. $C_{14}H_{22}ClO_2PS_2$. Calcd., %: C, 47.65; H, 6.28; P, 8.76.

Dichloroanhydride of 2-chloro-1-phenylthioethylthiophosphonic acid: b.p. 116–117°C/0.1 mm, d_4^{20} 1.4810, n_D^{20} 1.6440, δ_P 84 ppm. Found, %: C, 31.58; H, 2.63; P, 10.01. $C_8H_8Cl_3PS_2$. Calcd., %: C, 31.42; H, 2.62; P, 10.15.

Reaction of phenylsulfenyl chloride with isopropenyl- and styrylphosphonates. The interaction of phenylsulfenyl chloride with isopropenylphosphonates was conducted as described above. To complete the reaction with styrylphosphonates, the reaction mixture was maintained for 2–3 days at room temperature. The products of the reaction were distilled in vacuum.

Dichloroanhydride of 2-chloro-1-phenylthioisopropylphosphonic acid: b.p. 152–153°C/0.1 mm, d_4^{20} 1.4310, n_D^{20} 1.6012, δ_P 51 ppm. Found, %: C, 36.30; H, 3.32; P, 10.20. $C_9H_{10}Cl_3OPS$. Calcd., %: C, 36.61; H, 3.32; P, 10.62.

O,O-Dimethyl 2-chloro-1-phenylthioisopropylphosphonate: b.p. 124–126°C/0.1 mm, d_4^{20} 1.3383, n_D^{20} 1.6012, δ_P 28 ppm. Found, %: C, 45.12; H, 5.45; P, 10.35. $C_{11}H_{16}ClO_3PS$. Calcd., %: C, 44.82; H, 5.43; P, 10.53.

O,O-Diisopropyl 2-Chloro-1-phenylthioisopropylphosphonate: b.p. 155–158°C/0.1 mm, d_4^{20} 1.1701, n_D^{20} 1.5350, δ_P 19 ppm. Found, %: C, 51.37; H, 6.60; P, 8.29. $C_{15}H_{24}ClO_3PS$. Calcd., %: C, 51.35; H, 6.89; P, 8.83.

Dichloroanhydride of 2-chloro-2-phenyl-1-phenylthioethylphosphonic acid: m.p. 110–113°C (from CH_3CN), δ_P 44 ppm. Found, %: C, 46.93; H, 3.46; P, 8.20; Cl, 29.58; S, 8.91. $C_{14}H_{12}Cl_3OPS$. Calcd., %: C, 46.99; H, 3.31; P, 8.47; Cl, 29.09; S, 8.77.

O,O-Diisopropyl 2-chloro-2-phenyl-1-phenylthioethylphosphonate, light-yellow thick oil: n_D^{20} 1.5578, δ_P 18 ppm. The substance was multiply washed with pentane. Found, %: C, 58.06; H, 6.32; P, 7.87. $C_{20}H_{26}ClO_3PS$. Calcd., %: C, 58.18; H, 6.30; P, 7.51.

O,O-Dimethyl 2-chloro-2-phenyl-1-phenylthioethylphosphonate, light-yellow thick oil: δ_P 22 ppm. Found, %: C, 54.12; H, 5.11; P, 8.28. $C_{16}H_{18}ClO_3PS$. Calcd., %: C, 53.86; H, 5.05; P, 8.69.

Preparation of O,O-diisopropyl 1,2-dichloroisopropylphosphonate. Chlorine (0.01 mol) in 50 mL CCl_4 was added at room temperature to the equimolar amount of O,O-diisopropyl isopropenylphosphonate in 20 mL CCl_4. The mixture was maintained at room temperature for 4–5 hours till the colour faded out. The solvent was removed in vacuum and the residue distilled. B.p. 70–72°C/0.1 mm, d_D^{20} 1.1472, n_D^{20} 1.4503, δ_P 16 ppm. Found, %: C, 39.11; H, 7.07; P, 10.98. $C_9H_{19}Cl_2O_3P$. Calcd., %: C, 39.01; H, 6.91; P, 11.15.

Dehydrochlorination of adducts of phenylsulfenyl chloride and vinyl-phosphonates and -thiophosphonates. Ether solution of triethylamine (0.012 mol) was added dropwise at stirring to the solution of adduct (0.01 mol) in 10 mL abs. ether. The solution was left overnight and the precipitate filtered. As evidenced by ^{31}P NMR spectroscopy, in the case of vinylphosphonic acid, the products of dehydrochlorination undergo chemical conversions when distilled in vacuum.

Dichloroanhydride of 1-phenylthiovinylphosphonic acid: b.p. 105–106°C/0.1 mm, n_D^{20} 1.6194, δ_P 31 ppm. Found, %: C, 37.81; H, 2.77; P, 11.99. $C_8H_7Cl_2OPS$. Calcd., %: C, 37.94; H, 2.77; P, 12.25.

O,O-Diisopropyl 1-phenylthiovinylthiophosphonate: b.p. 110–112°C/0.01 mm, n_D^{20} 1.5492, δ_P 79 ppm. Found, %: C, 53.52; H, 6.70; P, 10.01. $C_{14}H_{21}O_2PS_2$. Calcd., %: C, 53.16; H, 6.64; P, 9.81.

Dichloroanhydride of 1-phenylthiovinylthiophosphonic acid: b.p. 98–100°C/0.01 mm, n_D^{20} 1.6240, δ_P 82 ppm. Found, %: C, 35.55; H, 2.63; P, 11.97. $C_8H_7Cl_2PS_2$. Calcd., %: C, 35.69; H, 2.60; P, 11.52.

Kinetic experiment. The kinetics of the addition of phenyl- and phosphonosulfenyl chlorides to unsaturated phosphonates was studied spectrophotometrically on a SF-26 instrument using thermostatted (±0.1°C) cells. The solvents were multiply distilled over driers. All experiments were carried out under argon. Rate constants of the reaction were calculated from pseudofirst order rate constants determined graphically or computed by the least squares method basing on the change of absorption of the initial sulfenyl chlorides. The operating wavelength was chosen by the absorption maxima of the initial sulfenyl chlorides and changed depending upon the solvent from 385 nm to 395 nm for phenylsulphenyl chloride and from 335 nm to 340 nm for phosphonosulfenyl chloride. The initial unsaturated phosphonates and the products of addition practically do not absorb within this range. The concentration of vinylphosphonates changed between 0.03–0.4 mol/L, of phenylsulfenyl chloride, 0.002–0.003 mol/L, and phosphonosulfenyl chloride, 0.02–0.04 mol/L. The reactions were completed to 25–85%. Rate constants were averaged over 2–4 experiments, the error did not exceed 3–5%.

Statistical processing of kinetic data was performed by the multivariate regression analysis on an Elektronika D3-28 computer.

REFERENCES AND NOTES

1. G. A. Kutyrev, A. I. Vinokurov, E. A. Ishmaeva, I. Kh. Shakirov, R. R. Shagidulin, R. A. Cherkasov and A. N. Pudovik, *Zh. Obshch. Khim.*, **49**, 524 (1979).
2. A. N. Pudovik and G. M. Denisova, *Zh. Obshch. Khim.*, **23**, 263, 267 (1953).
3. E. L. Gefter, *Uspekhi Khim.*, **25**, 162 (1956).
4. A. N. Nesmeyanov, M. I. Rybinskaya and A. V. Rybin, *Uspekhi Khim.*, **36**, 1089 (1967).
5. V. K. Promonenkov and S. Z. Ivin, *Uspekhi Khim.*, **37**, 157 (1968).
6. F. V. Bagrov and N. E. Galkina, *Zh. Obshch. Khim.*, **49**, 1772 (1979).
7. A. N. Pudovik and M. M. Zakharova, *Uchenye Zapiski Kazanskogo Universiteta*, **115**, 2 (1955).

8. A. N. Pudovik, I. V. Gurianova and E. A. Ishmaeva, "Organic compounds: Reactions and Investigation Methods," Collection No. 19, Moscow, Khimiya Publishers (1968) (in Russian).
9. H. Shenhav, Z. Rappoport and S. Patai, *J. Chem. Soc.*, **B**, 469 (1970).
10. G. A. Kutyrev, O. A. Raevskaya, R. A. Cherkasov and A. N. Pudovik, *Zh. Obshch. Chim.*, **44**, 746 (1974); N. V. Kashina, I. P. Lipatova, G. A. Kutyrev, R. A. Cherkasov and A. N. Pudovik, *Zh. Obshch. Khim.*, **44**, 504 (1974).
11. A. N. Pudovik, R. A. Cherkasov and G. A. Kutyrev, *Zh. Obshch. Khim.*, **43**, 1466 (1973).
12. A. N. Pudovik, R. A. Cherkasov and G. A. Kutyrev, *Dokl. AN SSSR*, **208**, 872 (1973).
13. M. I. Kabachnik, T. A. Balueva, T. Ya. Medved', E. N. Tsvetkov and Chzhan Zhunyui, *Kinetika i Kataliz*, **6**, 212 (1965).
14. Kh. M. Angelov, K. V. Bachkov, B. I. Ionin and M. Kirilov, *Zh. Obshch. Khim.*, **49**, 2438 (1979).
15. A. N. Pudovik, N. G. Khusainova and E. A. Berdnikov, *Dokl. AN SSSR*, **250**, 116 (1980).
16. N. G. Khusainova, L. V. Naumova, E. A. Berdnikov, G. A. Kutyrev and A. N. Pudovik, *Phosphorus and Sulfur*, **13**, 135 (1982).
17. G. A. Kutyrev, A. I. Vinokurov, R. A. Cherkasov and A. N. Pudovik, *Dokl. AN SSSR*, **245**, 880 (1979).
18. G. A. Kutyrev, A. I. Vinokurov, B. I. Istomin, R. A. Cherkasov and A. N. Pudovik, *Zh. Obshch. Khim.*, **51**, 1003 (1981).
19. I. V. Bodrikov, A. V. Borisov, L. V. Chumakov, N. S. Zefikov and W. A. Smit, *Tetrahedron Lett.*, **21**, 115 (1980).
20. I. V. Bodrikov, L. V. Chumakov, A. N. Pryadilova, N. S. Zefirov and W. A. Smit, *Dokl. AN SSSR*, **251**, 1409 (1980).
21. S. Z. Ivin and V. K. Promonenkov, *Zh. Obshch. Khim.*, **37**, 489 (1967).
22. L. P. Rasteikene and T. A. Praskene, *Trudy AN LSSR, ser. B*, **2**, 79 (1975); L. P. Rasteikene and V. I. Vidugirene, *Trudy AN LSSR, ser. B*, **5**, 37 (1975).
23. W. H. Mueller, R. M. Rubin and P. E. Butler, *J. Org. Chem.*, **31**, 3537 (1966).
24. W. A. Thaler, W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, **90**, 2069 (1969).
25. G. Högel and H. Dolhaine, *Phosphorus and Sulfur*, **3**, 47 (1977).
26. N. F. Chamberlain, "The Practice of NMR Spectroscopy (with Spectra-Structure Correlation for Hydrogen-1)," Plenum Press, New York, London, p. 98.
27. The individual regioisomer was obtained by prolonged maintaining of the reaction mixture at 40–50°C in the presence of HCl.
28. Yu. Yu. Samitov, A. A. Musina, R. M. Aminova, M. A. Pudovik, A. I. Khajarov and M. D. Medvedeva, *OMR*, **13**, 163 (1980).
29. L. P. Rasteikene, D. I. Greichute, M. G. Linkova and I. L. Knunyants, *Uspekhi Khim.*, **46**, 1041 (1977).
30. Yu. Yu. Samitov, Khimiya Geterotsiklicheskikh Soedinenii, 1587 (1978).
31. V. I. Zakharov, Yu. V. Belov, Yu. L. Kleiman, N. V. Markovin and B. I. Ionin, *Zh. Obshch. Khim.*, **44**, 1415 (1974); Yu. Yu. Samitov, *Zh. Obshch. Khim.*, **52**, 2211 (1982).
32. E. Kühle, *Synthesis*, **11**, 563 (1971); E. Kraweryk and A. Skowronska, *Phosphorus and Sulfur*, **9**, 189 (1980).
33. V. V. Zverev, Ya. Ya. Villem, L. V. Ermolaeva and A. F. Lisin, *Dokl. AN SSSR*, **246**, 1368 (1979).
34. T. A. Mastryukova and M. I. Kabachnik, *Uspekhi Khim.*, **38**, 1751 (1969).
35. M. Charton, *J. Org. Chem.*, **43**, 2383 (1978).
36. B. I. Istomin and V. A. Baransky, *Uspekhi Khim.*, **51**, 394 (1982).
37. G. H. Schmid and D. G. Garratt, *Can. J. Chem.*, **51**, 2463 (1973).
38. G. H. Schmid, C. L. Deand and D. G. Garratt, *Can. J. Chem.*, **54**, 1253 (1976).
39. L. P. Rasteikene, Z. A. Palaikite and V. -R. V. Talene, *Zh. Organ. Khim.*, **11**, 929 (1975).
40. G. H. Schmid and D. G. Garratt, *Tetrahedron Lett.*, **34**, 2869 (1978).
41. Y. Kikuzono, T. Yamabe, S. Nagato, H. Kato and K. Fukui, *Tetrahedron*, **30**, 2197 (1974).
42. Yu. G. Gololobov, L. F. Kasukhin, M. P. Ponomarchuk, Yu. I. Budilova *et al.*, Khimiya i primenenie FOS, Trudy VI Konf., Kiev, Naukova, Dumka Publishers, p. 179 (1981).
43. E. N. Tsvetkov, D. I. Lobanov and R. A. Malevannaya, Khimiya i Primenenie FOS, Trudy VI Konf., Moscow, Nauka Publishers, p. 85 (1972).
44. M. I. Kabachnik and T. Ya. Medved', *Izv. AN SSSR, OKhN*, 2143 (1959).
45. G. M. Kosolapoff, *J. Am. Chem. Soc.*, **70**, 1971 (1948).
46. L. N. Hamilton, Pat. USA No. 2365466. C.A. **39**, 4619 (1949).
47. K. N. Anisimova and A. N. Nesmeyanov, *Izv. AN SSSR, OkhN*, 1003 (1955).
48. M. I. Kabachnik and T. Ya. Medved', *Izv. AN SSSR, OkhN*, 604 (1961).
49. K. N. Anisimova and A. N. Nesmeyanov, *Izv. AN SSSR, OkhN*, 19 (1956).
50. K. N. Anisimova, A. N. Nesmeyanov and N. E. Kolobova, *Izv. AN SSSR OkhN*, 796 (1954).
51. K. Weygand and G. Hilgetag, "Organisch-chemische Experimentier kunst," Leipzig, Barth. (1964).