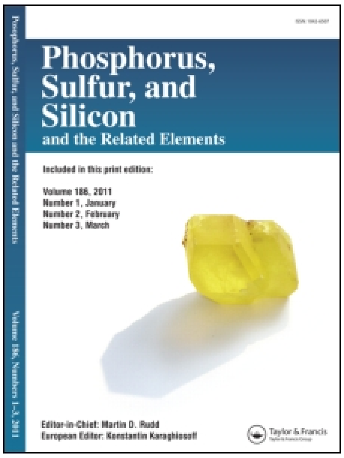

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ALKENYLSULFENYLCHLORIDES. II. INTERACTION OF γ,γ-DISUBSTITUTED PHOSPHORUS-CONTAINING ALLENES WITH SULFUR DICHLORIDE

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ALKENYLSULFENYLCHLORIDES. II. INTERACTION OF γ,γ-DISUBSTITUTED PHOSPHORUS-CONTAINING ALLENES WITH SULFUR DICHLORIDE

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Reactions of γ,γ-disubstituted allenylphosphonic acid derivatives and sulfur dichloride result in formation of various types of phosphorus-containing alkenylsulfenylchlorides depending on the nature of the substituents on the phosphorus atom and the allenic system. In particular, first sulfenylchlorides containing 1,3-alkadienyl moiety were obtained.

Keywords: allenylphosphonates; sulfur dichloride; electrophilic addition; alkenylsulfenylchlorides; 1,2-oxaphosphol-3-enes; 1,3-alkadienyl-1-phosphonates

INTRODUCTION

We have shown recently (short communications, see Ref 1) that interaction of sulfur dichloride with substituted allenes represents a new approach to alkenylsulfenylchlorides—scarcely studied and generally assumed to be exotic and unstable compounds[2]. Application of this approach to phosphorus-containing allenes had opened the way to 1,2-oxaphosphol-4-chlorothio-3-enes-heterocyclic sulfenylchlorides possessing a number of interesting features[3].

In order to investigate the scope and limitations of the new approach to unsaturated phosphorus-containing sulfenylchlorides we have studied interaction

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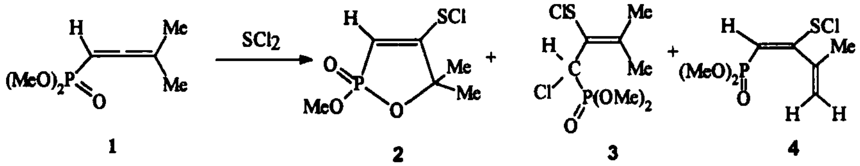
*Corresponding author.

of SCl_2 with several γ,γ-disubstituted allenylphosphonic acid derivatives having different substituents on the phosphorus atom and the allenic system.

RESULTS

Previously we reported that the reaction of α-unsubstituted allenylphosphonate **1** and SCl_2 resulted in oxaphospholene **2** formation as a major product (92–95%)[1]. The electrophilic cyclization with participation of phosphoryl oxygen is assumed to be typical for reactions of allenylphosphonates with electrophilic reagents and usually is reported to proceed with yields close to quantitative. However, we have noticed formation of minor amounts of two other products **3** and **4** (4–7% and 1–2% according to NMR spectra).

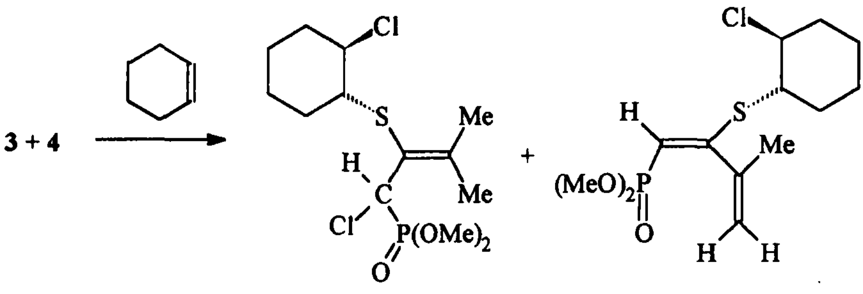


SCHEME 1

Spectral methods as well as chemical properties of the adducts indicated that the latter compounds were presumably new alkenylsulfenylchlorides, first one being the product of addition of SCl_2 to 1,2-double bond of the allenic system, second one having the 1,3-butadienyl skeleton.

These data were very intriguing because simultaneously **two** new alkenylsulfenylchlorides were formed. Especially interesting we have found the formation of **dienylsulfenylchloride 4**—the first dienylsulfenylchloride ever obtained (see: Discussion, part 2). That was why we have considered important to receive an unambiguous proof of the products structure and to find synthetic ways to the phosphorus-containing alkenylsulfenylchlorides with new structures.

The unsaturated sulfenylchlorides themselves turned out to be unstable species and in order to elucidate their structures we have transformed the compounds **3**, **4** into adducts with cyclohexene by treating the reaction mixture with cyclohexene in CCl_4. The reactions (Scheme 2) proceeded very smoothly and almost quantitatively as far as it can be judged by NMR spectra and TLC data. NMR spectra of both sulfenylchlorides **3**, **4**, and the adducts **5**, **6** were in good agreement with the proposed structures. For instance, the ^1H NMR spectrum of the dienes **4**, **6** contained a set of resonances characteristic for the isoprenyl group. The ^1H NMR spectrum of the 1,2-adduct displayed a signal for HCCl with relatively small J_{HP} (7 Hz for **3** and 2.6 Hz for **5**) and a signal for two methyl groups connected to a double bond. The ^{31}P chemical shifts of the minor products were typical for acyclic unsaturated phosphonates[4]. Unfortunately, the minor content of the new sulfenylchlorides in the reaction mixture made separation of adducts **5**, **6** from products of sulfenylchloride **2** addition rather tedious and a time-consuming task. Therefore, we have tried to find another, more efficient way to compounds **5**, **6**.



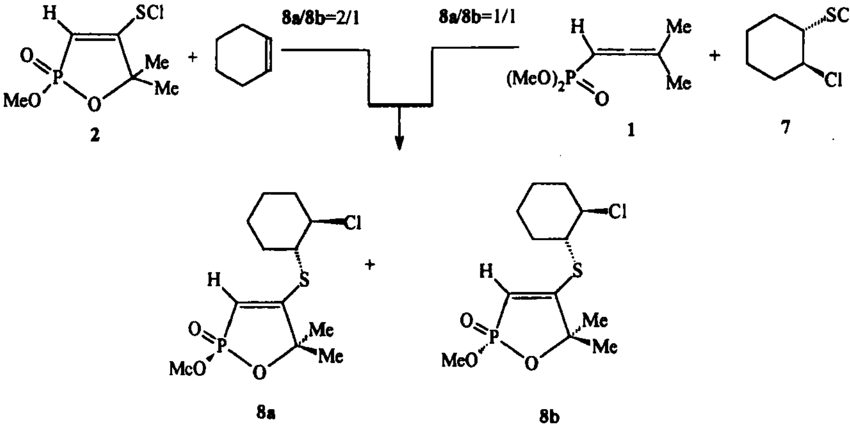
5 **6**

SCHEME 2

Bearing in mind that interaction of the allene **1** with an alkylsulfenylchloride could lead, in some cases, to 1,2-adducts[4a,b] and 1,3-alkadiene[4b], we have turned to the reaction of the allene **1** with sulfenylchloride **7**. Unfortunately, this reaction proceeded in more traditional direction and led to the formation of the diastereomeric 1,2-oxaphospholenes **8a,b** in the ratio 1 : 1[5] (these compounds we obtained previously by reaction of **2** with cyclohexene[1b,c]). Although the 1,2-adduct **5** was detected in reaction mixture, it was again a minor product, and the reaction mixture was contaminated with considerable amounts of bis-(2-chlorocyclohexyl)sulfide.

That was why we had tried the two-step approach to compounds **5** and **6** based on the reaction of SCl_2 with dichloroanhydride of allenylphosphonic acid **9**. Basing on the data from the literature[4,6] one could expect formation of the products with the desired skeleton which 1) would be of interest as new alkenylsulfenylchlorides; 2) could be transformed into compounds **5**, **6**.

The dichloroanhydride **9** reacted with SCl_2 relatively slowly the reaction required at least 6–8 hours to be completed at room temperature (for comparison, the reaction with the ester **1** was instantaneous). Nevertheless, after removing of solvent and excess of SCl_2 in vacuoa mixture of 1,2-adduct **10** and 1,3-alkadiene **11** as the two major products in the ratio 5 : 3 was obtained. Besides, the reaction mixture contained about 5–7% of the 2-chloro-butadiene **12**.

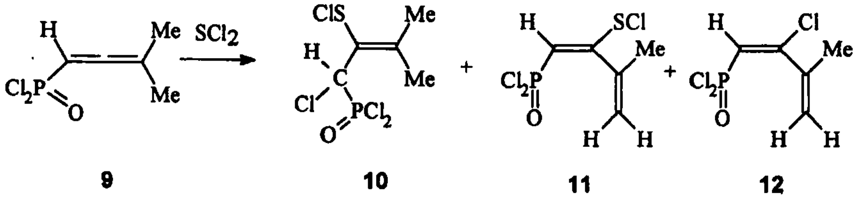


SCHEME 3

The synthetic potential of the compounds **10** and **11** is determined by the simultaneous presence of two highly reactive centres at phosphorus and sulfur.

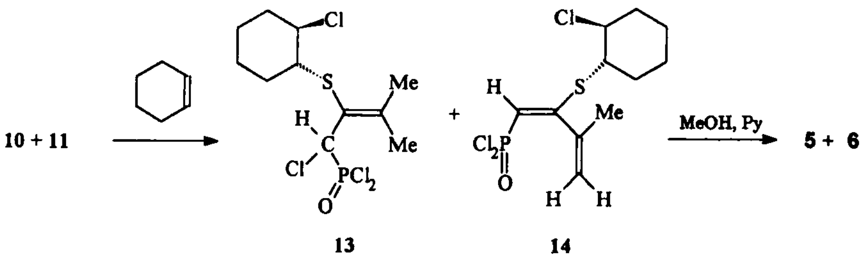
We have managed to carry out their step-by-step reactions with nucleophiles: for instance, the sulfenylchlorides easily reacted with cyclohexene to give the dichloroanhydrides of 2-(2-chlorocyclohexyl)thio-butenyl(butadienyl)phosphonic acids **13** and **14**, and the latter ones underwent the reactions typical for dichloroanhydrides of phosphonic acids, for example, the chlorine could be substituted by alkoxy groups by treatment with 2 moles of alcohol. As a result of this synthetic sequence, we have obtained the desired sulfides **5**, **6** and isolated them by means of column chromatography in a total 50% yield based on the starting allene **9** (14% for **6** and 35% for **5**) (Scheme 5).

Having established the structures of the phosphorus-containing alkenylsulfenylchlorides of two types (**3**, **10** and **4**, **11**) we continued the search for new alkenylsulfenylchlorides. Two substituted allenylphosphonates **15** and **17** which were known to be able to react with electrophiles with formation of different



10/11/12 = 5/3/0.3

SCHEME 4



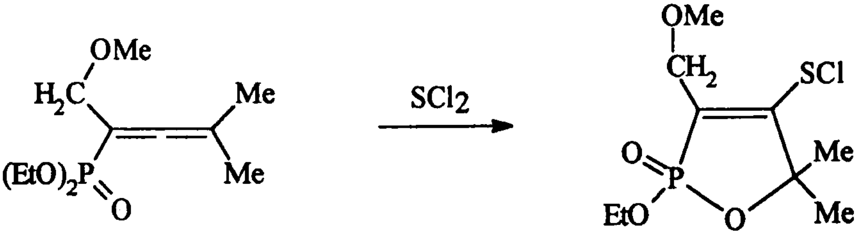
SCHEME 5

oxaphospholenes products[7] have been chosen for investigation. We have supposed that the reactions of these allenes with SCl_2 could expand the list of new phosphorus-containing alkenylsulfenylchlorides.

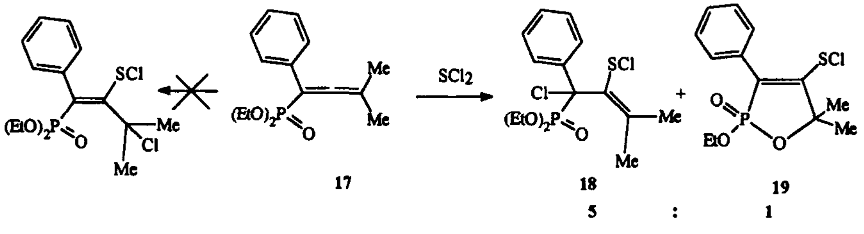
It was found that introduction of the methoxymethylene fragment had no influence on the direction of interaction with SCl_2. The reaction of allene **15** proceeded via cyclization with participation of the phosphoryl oxygen (as in the case of allene **1**) and gave oxaphospholene **16** as a sole product (isolated as cyclohexene adduct in 90% yield).

The structure of the adduct **16** was confirmed by the value of $^3J_{HP}$ (14Hz) observed for the CH_2-group from the methoxymethylene moiety (value of the analogous constants in dihydrofuranes is about 1–2 Hz[7a]), by relative integral intensities of other signals in the PMR spectra and by value of the ^{31}P NMR chemical shift (about 30 ppm) typical for oxaphosphol-3-enes[6a,b].

At the same time, the result of the reaction of allene **17** turned out to be dramatically different both from the results with other abovementioned allenes and from literature data[7b] reporting 2,3-adduct formation. The reaction resulted in the formation of the 1,2-adduct **18** as a major product. Oxaphospholene **19** was a minor product.



SCHEME 6



SCHEME 7

The structure of adduct **18** was unequivocally proved by its ^{1}H and ^{13}C spectra. In particular, very illustrative are ^{13}C NMR data given in the Experimental. ^{1}H NMR spectra are in good agreement with the proposed structure as well, for instance, the methyl groups are displayed as two doublets each of them corresponding to 3 protons. The coupling constants of these protons are characteristic for *cis* ($^{5}J_{HP}$ 4.0–4.4) and *trans* ($^{5}J_{HP}$ 5.6–6.0) position to the phosphorus atom[4].

DISCUSSION

1. Stability

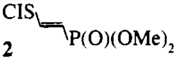
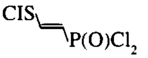
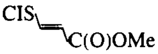
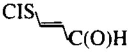
It is to be stressed that the stability of the alkenylsulfenylchlorides is only relative and all obtained sulfenylchlorides are highly reactive compounds that should be used in further reactions as soon as possible. Nevertheless, unsaturated sulfenylchlorides without perhalogenated groups are surprisingly rare compounds and this (even relative) stability is noteworthy.

Although the reasons of the relative stability of the phosphorus-containing alkenylsulfenylchlorides are not determined it seems reasonable to suppose that the main one is the influence of the electron-withdrawing phosphoryl group.

In order to confirm this supposition we have performed simple semiempirical quantum chemical calculations (AM1[8a], PM3[8b]) of several vinylsulfenylchlorides **2**, **23–25**, **28**, **29** (Tabl. I, II). Ethylsulfenylchloride **23**, ethene **21**, phosphorylsulfenylchlorides **26** and **27** were added for comparison.

The results should be treated as preliminary and used only as a rough guide because of some discrepancies between the figures given by the two methods[8c]. Nevertheless, the AM1 and PM3 results are in accord with each other in description of general tendencies and, therefore, can be used as a first approximation.

TABLE I Frontier molecular orbitals energies of alkenylsulfenylchlorides and related compounds

	HOMO, (eV)		*LUMO, (eV)*		*ΔE (HOMO/LUMO)*	
Compound	AM1	PM3	AM1	PM3	AM1	PM3
EtSCl (**20**)	—	—	−1.11	−1.17	—	—
Ethene (**21**)	−10.55	−10.64	—	—	—	—
 (**22**)	−8.32	−8.77	—	—	—	—
 (**23**)	−8.69	−9.11	−1.26	−1.28	7.43	7.83
	−9.62	−9.45	−1.93	−1.50	7.68	7.95
2	−9.63	−9.50	−2.05	−1.64	7.58	7.86
	−10.16	−10.08	−2.43	−2.05	7.73	8.03
$(MeO)_2P(O)SCl$ (**26**)	—	—	−1.89	−1.93	—	—
$Cl_2P(O)SCl$ (**27**)	—	—	−3.82	−3.28	—	—
	−9.17	−9.47	−1.73	−1.62	7.44	7.85
	−9.11	−9.43	−1.69	−1.58	7.42	7.85

The simplest vinylsulfenylchloride **23** is expected to be a more active nucleophile compared to ethene (nearly as active as methylthioethene) and a more and active electrophile compared to EtSCl. Thus, reaction of compound **23** "self-annihilation" by reaction of two molecules **23** (frontier orbitals energy gap 7.83 eV (PM3)) is likely to proceed more rapidly than the reaction of ethene and EtSCl (energy gap 9.47 eV (PM3)). Introduction of a phosphoryl group simultaneously lowered the energies of both occupied and unoccupied molecular orbitals (MO). The influence on the HOMO (including adjacent double bond, see: Fig. 1) is larger than on the remote SCl group (LUMO) which results in a small increase in the HOMO/LUMO energy gap. The effect is more pronounced in the case of $P(O)Cl_2$ group. Besides, considerable increase of double bond polarisation is found in the latter case which might contribute to the stability of phosphorus-containing vinylsulfenylchlorides (Table II).

Comparison of compounds **2**, **24**, and **25** LUMOs energies with data for phosphorylsulfenylchlorides **26**, **27** indicates that PM3 predictions seem to be more reliable in these cases. Based on PM3 data electrophilic activity is expected to increase in the following order: alkylsulfenylchlorides < vinylsulfenylchlorides < phosphorylsubstituted alkenylsulfenylchlorides **2**, **24**, **25** < phosphorylsulfenylchlorides.

LUMO and HOMO of sulfenylchlorides **23** and **25** are represented on Figure 1, frontier MOs of the sulfenylchlorides **2** and **24** are in general similar to those drawn below. It is clear that LUMO of vinylsulfenylchloride corresponds to the

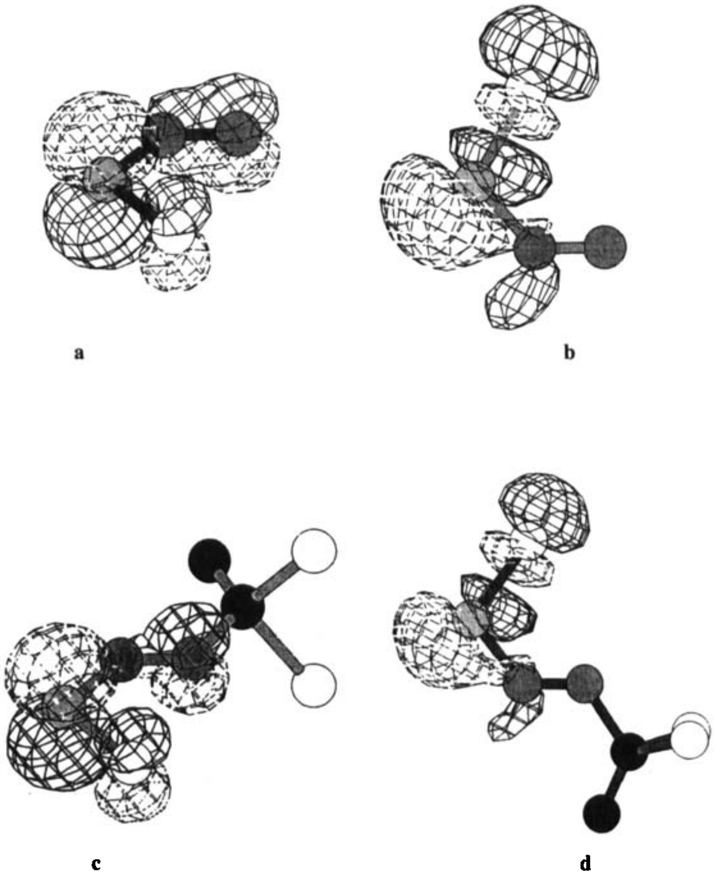


FIGURE 1 Frontier orbitals for compounds **23** and **25**. Solid and dashed lines correspond to negative and positive orbital contours. a) HOMO of **23**; b) LUMO of **23**; c) HOMO of **25**; d) LUMO of **25**.

TABLE II Charge Distribution in $\mathrm{RSC^1H{=}C^2HR'}$ group

	Charge on C^1		*Charge on C^2*	
Compound	*AM1*	*PM3*	*AM1*	*PM3*
22	−0.230	−0.235	−0.240	−0.169
23	−0.364	−0.282	−0.195	−0.105
24	−0.237	−0.163	−0.943	−0.547
2	−0.251	−0.204	−0.929	−0.573
25	+0.001	−0.114	−0.938	−0.672
28	−0.315	−0.204	−0.196	−0.178
29	−0.309	−0.195	−0.265	−0.253

SCl bond, whereas HOMO includes the double bond along with sulfur and chlorine p-orbitals. Introduction of the $P(O)Cl_2$ group has little influence on LUMO but considerably alters HOMO nature. Besides all vinylsulfenylchlorides should be more inert towards electrophilic reagents compared to **21** and **22** and the possibility of the reaction on sulfur instead of the double bond should be taken into consideration. Data obtained for compounds **28** and **29** indicate that other electron withdrawing substituents would probably have a similar influence on the stability and reactivity of vinylsulfenylchlorides although some differences could be expected.

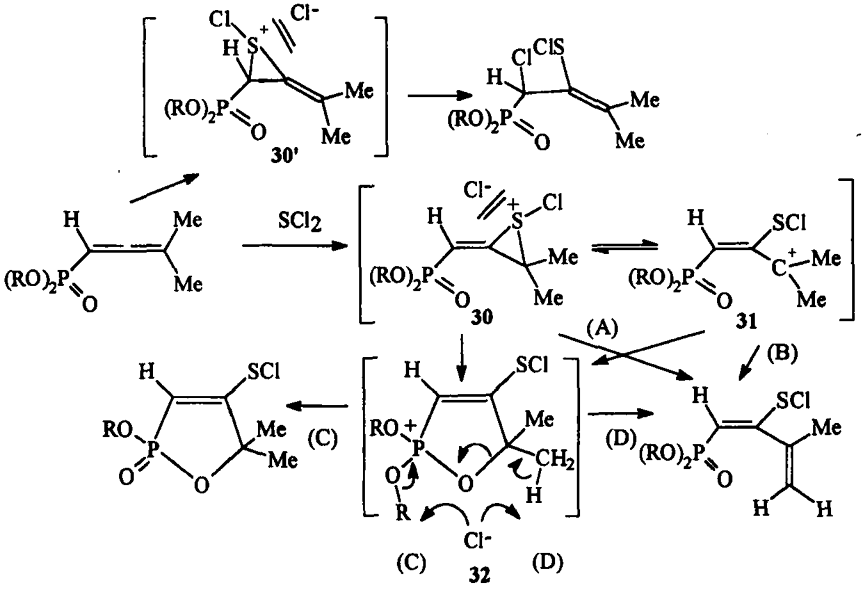
2. Formation of 1,3-Alkadienylsulfenylchlorides

Both formation and stability of the sulfenylchlorides **4** and **11**, containing the 1,3-alkadienyl moiety are noteworthy, because, to the best of our knowledge, compounds **4** and **11** are the **first sulfenylchlorides containing several double bonds**.

The reason can be easily understood: the most general previously known route to unsaturated sulfenylchlorides which is based on the reactions of SCl_2 with acetylenes could not be applied to dienylsulfenylchlorides synthesis because the reaction of sulfenylchlorides with vinylacetylenes leads to addition to the double bond instead of the triple bond[9]. In our case, there is no 3,4-double bond in the starting material and the second unsaturated fragment is formed **as the result of the reaction**! This example shows that the new approach to unsaturated sulfenylchlorides is an useful addition to the known ones.

Although there is an example of 1,3-alkadiene formation as the result of proton elimination from episulfonium ion **30** (or corresponding carbenium ion **31**)[10] (routes **A** and **B**), obviously another, specific for allenylphosphonates pathway **D**—elimination of hydrogen chloride from phosphonium salt **32**—accounts for the formation of the dienes **4** and **11** in the discussed reactions. This route is known to lead exclusively to formation of s-*cis*-1,3-butadiene[6a,b] (unlike from other known routes to 1,3-butadienylphosphonates[6c,d]) and in this case the 3,4-double bond of 1,3-alkadienylsulfenylchloride should be remote from sulfur and thus the intramolecular cyclization is unfavored[11].

This route was well established for dichloroanhydrides of allenylphosphonic acids[6a,b]. Now we have shown that 1,3-alkadienes **10, 11** formed from the dichloroanhydrides could be transformed to 1,3-alkadienes **5, 6** formed from esters of allenylphosphonic acids and, therefore, we have proved for the first time that in the case of the esters the formation of the dienes proceeds from phosphonium salt **32** as well.



SCHEME 8

3. Regioselectivity

Addition to a deactivated 1,2-double bond towards electrophilic attack in the reactions of allenylphosphonic acid derivatives with electrophiles is highly unusual; it was observed earlier only in reactions with some alkylsulfenylchlorides[4]. The traditional reaction scheme includes attack to the 2,3-double bond followed by oxaphospholene formation[6a,b,12]. Recently it was found that in some cases an alternative directions of cyclization could be observed[7,12c]. Nevertheless, in these cases the usual regioselectivity is preserved: the electrophilic reagents add to the 2,3-double bond of the allenic system.

In principle, the change of regioselectivity in the case of phenylsubstituted allene **17** could be attributed to possible stabilisation of the positive charge on the α-carbon by the phenyl group. In addition, steric influence of the phenyl group might preclude electrophilic attack *anti* to the phosphoryl group which is necessary for oxaphospholene formation. At the same time, addition of halogens and proton acids to the allene **17** proceeds exclusively with oxaphospholene formation[13] and the abovementioned factors in these cases seem to be unimportant which allows to suppose that the unusual course of the reaction is determined by the nature of the electrophilic reagent, whereas structural features of the allenes are less important (just tuning). The situation seems to be even more complicated in the case of dichloroanhydride **9** where both abovementioned factors beneficial for 1,2-bond addition are absent. Moreover, in comparison with the results of the reaction with allene **1** the result seems rather puzzling. The rise in electronegativity of a substituent near double bond favours the addition to this bond!

Previously it was suggested[4c] that the observed anomalous regioselectivity could be explained by an intermediate formation of the episulfonium ions **30, 30′** (which are not strongly influenced by electronic factors) and their stability in comparison with the open cations **31**. This suggestion seems rational, but if it were the case one could expect 1,2-adduct formation in the reaction with selenenylchlorides which is known to proceed via analogous cyclic ions. At the same time, the latter reactions unlike the reactions with sulfenylchlorides proceed exclusively across the 2,3-double bond. Therefore, it seems reasonable to suggest that the anomalous regioselectivity cannot be explained by assuming cyclic intermediates formation but rather lies in some peculiarities[14,15] of these intermediate structures which are present in the case of sulfenylchlorides.

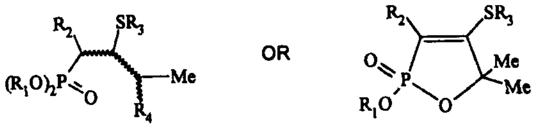
EXPERIMENTAL

NMR ^{1}H, ^{13}C and ^{31}P spectra were obtained in $CDCl_3$ (unless otherwise specified) at 200 and 81 MHz, chemical shifts are referenced to TMS and 85-% H_3PO_4 (ext.) respectively (Table III and Table IV). IR spectra were taken on Bruker IFS-113 (in CCl_4). Semiempirical calculations were carried out with full

TABLE III ^{31}P-NMR and IR spectral data

No.	*^{31}P (ppm)*	*P=O (cm^{-1})*	*C=C (cm^{-1})*
2	31.8	1272	1557
3	18.0	—	—
4	16.5	—	—
5	15.6	1253	1558
6	18.0	1246	1635, 1565
8a,b	35.1, 35.3	1264	1555
10	24.1	1275	1580
11	21.1	1285	1590, 1555
13	23.6	1275	1575
14	22.15	1280	1600, 1565
16	31.6	1264	1596
18	15.6	1258	1586
19	30.6	1260	1596

TABLE IV ^1H NMR data for



No.	*R₁*	*R₂*	*R₃*	*R₄*	*Me*
2	3.8 d(3H, 14Hz)	5.95 d(1H, 26Hz)	—	—	1.6 s; 1.55 s (6H)
3	3.6 d(6H, 12Hz)	5.7 d(1H, 7Hz)		2.3 br.s (3H)	2.05 br.s(3H)
4	3.6 d(6H, 12Hz)	5.6 d(1H, 14Hz)	—	5.5 br.s(1H); 5.3 br.s(1H)	2.2 br.s(3H)
5	3.7 d(6H, 12Hz)	5.15 d(1H, 2.6Hz)	4.1 ddd[a](1H); 3.1 ddd[a] (1H); 2.3–1.4 m(8H)	—	1.9 br.s[b]6H)
6	3.7 d(6H, 10Hz)	5.45 d(1H, 14Hz)	4.0 ddd[c] (1H); 3.2 ddd[c] (1H); 2.5–1.6 m(8H)	5.1 br.s (1H)[d], 5.05 br.s (1H)	1.85 s (3H)
8a	3.8 d(6H, 12Hz)	5.6 d(1H, 26Hz)	4.1 ddd[e] (1H); 3.8 ddd[e] (1H); 2.5–1.6 m(8H)	—	1.65 s; 1.55 s (6H)
8b	3.8 d(6H, 12Hz)	5.6 d(1H, 26Hz)	4.2 ddd[f] (1H); 3.85 ddd[f] (1H); 2.3–1.4 m(8H)	—	1.65 s; 1.55 s (6H)
10	—	6.0 d(1H, 16Hz)	—	—	2.2 s (6H)
11	—	5.9 d(1H, 27Hz)	—	5.4 br.s. (1H); 5.25 br.s. (1H)	2.1 s (3H)
13	—	5.4 d(1H, 18Hz)	4.0 m(1H); 3.05 m(1H), 2.3–1.2 m (8H)	—	1.9 s (6H)
14	—	5.7 d(1H, 30Hz)	3.9 m (1H); 3.05 m (1H); 2.3–1.2 m (8H)	5.15 br.s. (1H); 5.05 br.s. (1H)	1.85 s (3H)
16	4.3–4.0 m(2H); 1.4 t(3H, 7Hz)	4.4 d(2H, 14Hz); 3.5 s(3H)	—	—	1.6 d(6H, 8Hz)
18[g]	4.2–3.5 m(4H); 1.3 t (3H, 7 Hz); 1.1 t (3H, 7Hz)	7.7–7.1 m (5H)			2.2 d(3H, 4Hz); 1.6 d(3H, 6Hz)
19	4.3–4.0 m (2H); 1.4 t(3H, J = 7)	7.7–7.1 m (5H, Ph)	—	—	1.5 c (3H, Me); 1.6 c (3H, Me)

[a] $J_1 = J_2 = 6.2, J_3 = 4.0$ (Hz). [b] 1.88 s and 1.85 s in CCl_4. [c] $J_1 = J_2 = 6.5, J_3 = 3.5$ (Hz). [d] In CD_3CN − q, 1.5 Hz. [e] $J_1 = J_2 = 7, J_3 = 3.8$ (Hz). [f] $J_1 = J_2 = 5.6, J_3 = 3.5$ (Hz). [g] ^{13}C NMR for **18**: δ, ppm, J, Hz, (±1Hz): 165.5 (10.9), 138.8 (4.1), 131.5, 128.5 (5.4), 128.3, 127.6, 75.0 (165.5), 64.0 (7.5), 63a) $J_1 = J_2 = 6.2, J_3 = 4.0$ (Hz). [b] 1.88 s and 1.85 s in CCl_4. [c] $J_1 = J_2 = 6.5, J_3 = 3.5$ (Hz). [d] In CD_3CN − q, 1.5 Hz. [e] $J_1 = J_2 = 7, J_3 = 3.8$ (Hz). [f] $J_1 = J_2 = 5.6, J_3 = 3.5$ (Hz). [g] ^{13}C NMR for **18**: δ, ppm, J, Hz, (±1Hz): 165.5 (10.9), 138.8 (4.1), 131.5, 128.5 (5.4), 128.3, 127.6, 75.0 (165.5), 64.0 (7.5), 63.6 (7.5), 27.2, 25.2, 16.3 (6.8), 16.2 (6.8).

geometry optimization until reaching RMS gradient of 0.01 kcal/mol E. Data for vinylsulfenylchlorides, vinylsulfides[16], vinylphosphonates[12b] are given for s-cis conformations.

All obtained sulfenylchlorides were fully characterised as cyclohexene adducts including NMR, IR, mass-spectra and combustion analysis. The results of these reactions, in particular, stereo- and diastereoselectivity as well as properties of the adducts (conformation equilibrium etc.) will be reported separately.

The procedure for reactions of SCl_2 with allenes 1, 14, 16: To a stirred solution of 1.5 eq of SCl_2 in CCl_4 at 5–10°C a solution of an allene was slowly added and the mixture was stirred at this temperature for 15 minutes and at r.t. for half an hour. Then the excess of SCl_2 and solvent were removed in vacuo affording a mixture of compounds **2–4** (for allene **1**), **15** (for **14**), **17, 18** (for **16**) as viscous yellow liquids which were directly used for further reactions. The compounds **3, 15, 17** could be isolated by careful precipitation from CCl_4 solution with hexane.

Reaction of SCl_2 with 1-dichlorophosphoryl-3-methyl-1,2-butadiene. To a solution of freshly distilled SCl_2 (1.1 eq) in CCl_4 1 eq of the allene was added dropwise at 10°C, stirred for 24 h at 20°C. The excess of SCl_2 and the solvent were removed in vacuo, the reaction mixture was kept in vacuo (5–10 mm Hg) for an hour. A mixture of the compounds **9** and **10** was obtained, which was used in further transformations without purification.

Reactions of the compounds 11 and 12 with MeOH. To a solution of 1.0 eq of the dichloroanhydrides **11** and **12** in Et_2O a mixture of 2.05 equivalents of MeOH and 2 eq of pyridine was added dropwise at $-10-5$°C and the mixture stirred for 20 min at 20°C. The precipitate of amine hydrochloride was filtered and washed 2–3 times with small portions of Et_2O. The solvent was evaporated in vacuo and the residue was chromatographed (Silpearl, 40/100, eluent: hexane-ethylacetate, gradient from 4 : 1 to 1 : 2).

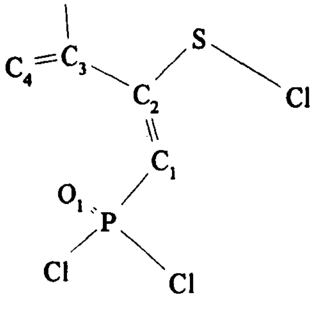


FIGURE 2 PM3 optimized geometry of the 1,3-butadiene **4**.

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