TABLE III

NMR DATA FOR THE DIBROMIDES AND DIAZIDES IN τ UNITS (CARBON TETRACHLORIDE)

Compd	Position CH_3	 CH_2	 CH	 CH=C
cis-1,4-Dibromo-2-butene	...	5.94, 6.06	...	4.02, 4.12, 4.21
cis-1,4-Diazido-2-butene	...	6.08, 6.17	...	4.09, 4.17, 4.25
trans-1,4-Dibromo-2-butene	...	6.05, 6.15	...	4.04[a]
trans-1,4-Diazido-1-butene	...	6.15, 6.20 (shoulder)	...	4.19[a]
3,4-Diazido-2-butene	...	6.69, 6.79	5.83, 5.93, 6.03	[b]
trans-1,4-Dibromo-2,3-dimethyl-2-butene	8.10	6.08	...	...
trans-1,4-Diazido-2,3-dimethyl-2-butene	8.13	6.17	...	...
3,4-Diazido-2,3-dimethyl-1-butene	8.18, 8.55	6.71	...	4.90

[a] This is the principal peak; other peaks are also present. [b] This terminal vinyl group is very complicated and contains too many peaks to list.

a diamine[18] whose dipicrate derivative gave the correct analysis for $C_{18}H_{22}N_8O_{14}$, mp 197.5°.

Anal. Calcd for $C_{18}H_{22}N_8O_{14}$: C, 37.64; H, 3.86; N, 19.51. Found: C, 37.21; H, 4.14; N, 19.67.

The purities of the diazides were determined to be approximately 95%, with the exception of 3,4-diazido-2,3-dimethyl-1-butene (VII) which contained 10% of VIII.

Stabilities of the Diazides.—Although equilibrium mixtures of IV and V had been distilled many times and were found to be stable to 130°, distillation of a sample for the final experiment of this study resulted in a violent explosion. No explanation can be given for the explosion. These compounds should be considered *extremely* hazardous. The equilibrium mixture of VII and VIII did not explode when heated to 190°. A violent explosion did occur, however, when they were heated in an open flame.

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[18] Vapor phase chromatographic analysis of this diamine product, on the same column as was used for the 1,4- and 1,2-butanediamines, indicated only one compound, whereas the chromatogram of the reduction product of VIII contained two peaks. These results indicate that reduction of the equilibrium mixture of VII and VIII gives pure 2,3-dimethyl-1,2-butanediamine and reduction of VIII gives a mixture of the isomeric diamines. Perhaps the rate of reduction of VIII is slow compared to that of VII, and VIII rearranges to VII which is rapidly reduced.

The Addition of O,O′-Dimethylphosphorylsulfenyl Chloride to Unsaturated Hydrocarbons

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O,O′-Dimethylphosphorylsulfenyl chloride was added to ethylene, propylene, pentene-1, isobutylene, 1,3-butadiene, isoprene, methylacetylene, and allene. The exclusive formation of O,O′-dimethyl S-chloroalkylthiophosphates was observed. Both Markovnikov- and anti-Markovnikov-oriented adducts were obtained from terminal olefins and conjugated dienes. Addition to the dienes produced exclusively 1,2-addition products. Allene and methylacetylene, however, afforded only anti-Markovnikov adducts.

Many O,O,S-trialkyl thiophosphates have been found to be of potential interest as pesticides[3] and, therefore, their chemistry and their preparation *via* displacement reactions[4] have been studied extensively. However, addition reactions to unsaturated hydrocarbons, an equally interesting approach to such compounds, have received little attention. In a previous study we have determined the scope and limitation of the cationic addition of dialkyldithiophosphoric acid to unsaturates.[5] Our present paper is primarily concerned with the adduct orientation obtained from dimethylphosphorylsulfenyl chloride, $(CH_3O)_2P(O)SCl$, and unsaturated hydrocarbons. Michalski and co-workers have reported the first additions of dialkylphosphorylsulfenyl chlorides to terminal olefins.[6,7] A similar addition to allene was described in the patent literature,[8] and most recently the addition of O,O-diethylphosphorylsulfenyl chloride to butadiene has been reported.[9]

Publication of the latter work on butadiene prompts us to report our results in this area. With the aid of nmr spectroscopy we were able to reveal a more complex picture of the adduct orientation. In contrast to the earlier claimed[6] exclusive formation of Markovnikov-oriented products we find little or no selectivity. An exception is the selective anti-Markovnikov addition to allene and methylacetylene.

In this study, O,O′-dimethylphosphorylsulfenyl chloride was chosen as a convenient model reagent for the important nmr analyses of the products. As typical olefin substrates, ethylene, propylene, pentene-1, isobutylene, 1,3-butadiene, isoprene, and allene were selected. Methylacetylene was used as a representative acetylenic compound.

Results

O,O′-Dimethylphosphorylsulfenyl chloride was prepared in high yield (>90%) by treating trimethyl phosphorothionate with 1 mole equiv of sulfuryl chloride.

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[1] Present address: Yale University, New Haven, Conn., summer employee, 1965.

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[3] G. Schrader, "Die Entwicklung neuer Insektizider Phosphorsäure-Ester," Verlag Chemie GMBH, Weinheim, Germany, 1963.

[4] K. Sasse, "Methoden der Organischen Chemie," Houben-Weyl, Vol. XII/2, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1964, pp 652–681.

[5] W. H. Mueller and A. A. Oswald, *J. Org. Chem.*, **31**, 1894 (1966).

[6] B. Borecka, T. Kapecka, and J. Michalski, *Roczniki Chem.*, **36**, 87 (1962).

[7] J. Michalski, B. Pliszka-Krawiecka, and A. Skowronska, *ibid.*, **37**, 1479 (1963).

[8] Y. G. Gololobov, V. V. Semidetko, and L. Z. Soborovskii, Russian Patent 166692 (1964).

[9] A. N. Pudovik and E. A. Ishmaeva, *Zh. Obshch. Khim.*, **35**, 2080 (1965).

TABLE I

O,O-DIMETHYLPHOSPHORYLSULFENYL CHLORIDE UNSATURATE MONOADDITIONS AND SOME PHYSICAL-ANALYTICAL DATA OF THE PRODUCTS, $(CH_3O)_2P(O)SR$

Olefin	Moles of olefin/ mole of sulfenyl chloride	General procedure	Yield,[a] %	Adduct												
				Selectivity for adduct[a] I:II	Structure I, R	Structure II, R	Summary formula	Bp uncorr, °C (mm)	Elemental compositon							
									Calculated, %				Found, %			
									C	H	P	S	C	H	P	S
Ethylene	>5:1	B	25	100	$\mathrm{CH_2CH_2Cl}$		$C_4H_{10}ClO_3PS$	82.5 (0.30)	23.48	4.93	15.14	15.67	23.60	4.85	14.62	15.95
Propylene	>5:1	B	29	51:49	$\underset{\mathrm{CH_3}}{\underset{\vert}{\mathrm{CH}}}\mathrm{CH_2Cl}$	$\mathrm{CH_2}\underset{\mathrm{Cl}}{\underset{\vert}{\mathrm{CH}}}\mathrm{CH_3}$	$C_5H_{12}ClO_3PS$	83.5 (0.30)	27.47	5.53	14.17	14.67	27.58	5.29	13.97	14.90
Pentene-1	5:1	A	71[b]	65:35	$\underset{\mathrm{CH_2Cl}}{\underset{\vert}{\mathrm{CH}}}\mathrm{C_3H_7}$	$\mathrm{CH_2}\underset{\mathrm{Cl}}{\underset{\vert}{\mathrm{CH}}}\mathrm{C_3H_7}$	$C_7H_{16}ClO_3PS$	94 (0.004)	34.08	6.54	12.56	13.00	34.27	6.41	12.24	13.10
Isobutylene	5:1	C	21	24	$\mathrm{CH_2}\underset{\mathrm{CH_3}}{\underset{\vert}{\mathrm{C}}}\mathrm{{=}CH_2}$		$C_6H_{13}O_3PS$	60–66 (0.002)	36.73	6.68	15.79	16.34	36.51	6.65	15.68	16.84
			69	57:19	$\mathrm{CH_2}\underset{\mathrm{Cl}}{\underset{\vert}{\mathrm{C}}}\mathrm{(CH_3)_2}$	$\underset{\mathrm{CH_2Cl}}{\underset{\vert}{\mathrm{C}}}\mathrm{(CH_3)_2}$	$C_6H_{14}ClO_3PS$	69.5–72 (0.003)	30.97	6.07	13.31	13.78	30.30	6.09	13.05	
Butadiene	5:1	C	97	73:27	$\mathrm{CH_2}\underset{\mathrm{Cl}}{\underset{\vert}{\mathrm{CH}}}\mathrm{CH{=}CH_2}$	$\underset{\mathrm{CH_2Cl}}{\underset{\vert}{\mathrm{CH}}}\mathrm{CH{=}CH_2}$	$C_6H_{12}ClO_3PS$	104–106 (0.025)	31.24	5.24	13.43	13.90	30.97	5.62	13.14	13.95
Isoprene	5:1	A	59[b]	65:35	$\mathrm{CH_2}\underset{\mathrm{Cl}}{\underset{\vert}{\mathrm{CH}}}\underset{\mathrm{CH_3}}{\underset{\vert}{\mathrm{C}}}\mathrm{{=}CH_2}$	$\underset{\mathrm{CH_2Cl}}{\underset{\vert}{\mathrm{CH}}}\mathrm{C(CH_3){=}CH_2}$	$C_7H_{14}ClO_3PS$	117–120 (0.0005)	34.33	5.72	12.66	13.10	34.59	5.76	11.88	13.22
Methylacetylene	5:1	C	45[b]	71:29	$\underset{\mathrm{CH_3}}{\underset{\vert}{\mathrm{C}}}{=}\underset{\mathrm{Cl}}{\underset{\vert}{\mathrm{CH}}}$	$\underset{\mathrm{CH_3}}{\underset{\vert}{\mathrm{C}}}{=}\underset{\mathrm{H}}{\underset{\vert}{\mathrm{CCl}}}$	$C_5H_{10}ClO_3PS$	74–77 (0.22)	27.72	4.65	14.30	14.80	27.57	4.60	13.62	14.71
Allene	5:1	C	53[b]	100	$\underset{\mathrm{CH_2Cl}}{\underset{\vert}{\mathrm{C}}}\mathrm{{=}CH_2}$		$C_5H_{10}ClO_3PS$	84.5–86 (0.24)	27.72	4.65	14.30	14.80	27.50	4.67	14.44	14.76

[a] Based on the weight and semiquantitative nmr analysis of the crude reaction products. [b] Theoretical yield is based on quantity of $PS(OCH_3)_3$ used since the sulfenyl chloride was not isolated.

TABLE II

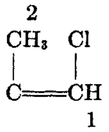
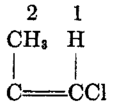
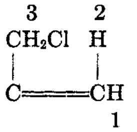
NMR PARAMETERS OF O,O-DIMETHYLPHOSPHORYLSULFENYL CHLORIDE–OLEFIN ADDUCTS, $(CH_3O)_2P(O)SR$

Starting olefin	R: Group structure 1 2 3 4	R: Group chemical shifts, ppm 1	2	3	4	J_{PSCH}, cps
Ethylene	$CH_2—CH_2Cl$	Dt[a] 3.13[b]	t 3.75[b]			17.5
Propylene	$CH\ \ (CH_3)—CH_2Cl$	m ~3.6	d 1.47[c]	d 3.77		
	$CH_2—CH(Cl)—CH_3$	Dd 3.10[d]	Tq 4.21[d]	d 1.58		15.5
Pentene-1	$CH\ \ (CH_2Cl)—CH_2CH_2—CH_3$	m *ca.* 3.7	d 3.75[d]	m ~1.69	t 0.98	
	$CH_2—CH(Cl)—CH_2CH_2—CH_3$	Dd 3.13	p ~3.98[d]	m ~1.69	t 0.98	15.5
Isobutene	$CH_2—C(CH_3)_2—Cl$	d 3.25	s 1.66			12.7
	$C(CH_3)_2—CH_2Cl$	d 1.55[e]	s 3.91			
	$CH_2—C(CH_3)=CH_2$	d 3.44	m 1.86	5.02 m 4.88		14.0
Butadiene	$CH_2—CH(Cl)—CH=CH_2$	Dd 3.19	q 4.58[f]	m ~5.8	m ~5.4	15.5
	$CH\ \ (CH_2Cl)—CH=CH_2$	m ~3.9	d 3.79	m ~5.8	m ~5.4	
Isoprene	$CH_2—CH(Cl)—C(CH_3)=CH_2$	Dd 3.18	t 4.59[g]	m 1.82	q 5.03[h] q 5.13[h]	15.7
	$CH\ \ (CH_2Cl)—C(CH_3)=CH_2$	m 3.75[i]	t 4.01[i]	m 1.82	q 5.03[h] q 5.13[h]	

[a] D, doublet of; T, triplet of; s, singlet; d, doublet; t, triplet; q, quartet; p, pentuplet; m, multiplet. [b] $J_{CH_2CH_2} = 7.5$ cps. [c] $J_{CHCH_3} = 6.5$ cps. [d] $J_{CH_2CH} = J_{CHCH_3} = 6.5$ cps. [e] $J_{PSCCH} = 1.5$ cps. [f] $J = 6.7$ cps. [g] $J_{CH_2CH} = 7.5$ cps. [h] $J_{C(CH_3)-CH_2}$ = *cis* < 0.5 cps, *trans* ~ 1.1 cps. [i] $J_{PSCHCH_2} = 6.7$ cps.

TABLE III

NMR PARAMETERS OF O,O′-DIMETHPHOSPHORYLSULFENYL CHLORIDE–ALLENE AND –METHYLACETYLENE ADDUCTS, $(CH_3O)_2P(O)SR$[a]

R: Group structure	Proton	Chemical shift, ppm	J, cps
 $\overset{2}{CH_3}(C)=\underset{1}{CH}(Cl)$	1	Qd 6.54	$J_{PSC-CH} = 5.0$; $J_{HC-CCH} = 1.5$
	2	Dd 2.17	$J_{PSCCH} = 3.0$
 $\overset{2}{CH_3}(C)=CCl(\overset{1}{H})$	1	Qd 6.06	$J_{PSCH-CH} = 7.2$; $J_{HC-CCH} = 1.1$
	2	Dd 2.24	$J_{PSCCH} = 3.0$
 $\overset{3}{CH_2Cl}(C)=\underset{1}{CH}(\overset{2}{H})$	1	Td 5.98	$J_{PSC-CH} = 3.50$; $J_{H_2C-} = 0$; $J_{HC-CCH} = 1.35$
	2	d 5.77	$J_{PSC-CH} = 4.1$; $J_{HC-CCH} = 0.65$
	3	Dd 4.32	$J_{PSCCH} = 1.93$

[a] Letters have the same meaning as in Table II; Q, quartet of.

The reaction temperature was kept below 0°. Removal of the gaseous products under high vacuum afforded the pure sulfenyl chloride. This procedure affords higher yields and higher product purity than the preparation described by the original workers.[7]

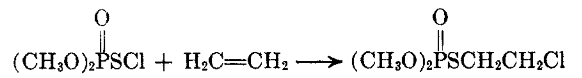
At first this sulfenyl chloride was allowed to react with gaseous olefins by bubbling the gas through it, but later it was found that better yields resulted if the sulfenyl chloride was dropped slowly into a solution of the gas in methylene chloride. Reaction temperatures were kept 10–15° below the boiling points of the olefins. Additions to liquid olefins were run without solvent at 0°.

All reactions were brought slowly to room temperature after the additions were completed and any solvents were removed under reduced pressure. The acidic mixtures were taken up in ether, neutralized, washed, dried, and the ether was removed under reduced pressure. The resulting crude products were analyzed by a combination of gas–liquid partition chromatography (glpc) and nuclear magnetic resonance spectroscopy (nmr). The products were further purified by fractional distillation *in vacuo* and the distilled products were also analyzed by glpc and nmr. In no instance could the positional isomers be separated by distillation.

Physical data and yields for the reactions are tabulated in Table I. Nmr parameters for the products are tabulated in Tables II and III.

In all cases, the nmr spectra of the addition products show that S alkylation occurs exclusively. The chemical shift values and the large spin–spin coupling constants (12.7–17.5 cps) observed are characteristic for the PSCH system and rule out the presence of $(CH_3O)_2P(S)OR$ structures in any amount detectable by nmr. The corresponding coupling for the POCH system is usually <13 cps. This selective attack to form the thiolphosphate corresponds with results found earlier in a study of the addition of O,O-diethylthiophosphoric acid to olefins.[5] A special characteristic of these spectra is the additional splitting of the protons on the α carbon owing to coupling to the phosphorus nucleus ($I = 1/2$) through the PSC or POC bonds. Therefore, the O-methyl protons in O,O′-dimethyl thiophosphates appear as a doublet. Further confirmation of the PSC structure of the adducts is found in the fact that the protons adjacent to sulfur appear at a considerably higher field than the corresponding protons of a POC system. This difference in chemical shift (1.52 ppm) was demonstrated in the spectrum of O,O′-S-trimethyl thiophosphate (OCH_3: $\delta = 3.75$ ppm, $J_{POCH} = 12.5$ cps; SCH_3: $\delta = 2.23$ ppm, $J_{PSCH} = 15.0$ cps). A strong infrared absorption at 1255 cm^{-1} owing to the P=O stretching vibration[10a] confirmed the thiol ester structure of the adducts.

Ethylene.—The addition of O,O′-dimethylphosphorylsulfenyl chloride (I) to ethylene led exclusively to the S-alkyl product, O,O′-dimethyl S-2-chloroethylthiophosphate (II), identified by its characteristic nmr

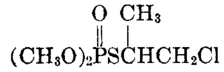


$$(CH_3O)_2\overset{\overset{O}{\|}}{P}SCl + H_2C{=}CH_2 \longrightarrow (CH_3O)_2\overset{\overset{O}{\|}}{P}SCH_2CH_2Cl$$

I II

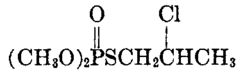
spectrum, and a $n^{24}\mathrm{D}$ of 1.4892 identical with that reported earlier.[7] Since no structural isomers are possible, this system was ideal to determine the possibility of O *vs.* S alkylation by nmr techniques. The triplet of a doublet appearing at 3.13 ppm ($J_{PSCH} = 17.5$ cps) was assigned to the α-methylene protons of the product which were split by spin–spin coupling with the β protons and the phosphorus nucleus. This confirmed the S-alkyl structure of the product since any O-alkyl product would have shown this signal shifted considerably downfield.

Propylene.—Treatment of propylene with I yielded a mixture of O,O′-dimethyl S-1-chloroisopropylthiophosphate (III) and O,O′-dimethyl S-2-chloropropylthiophosphate (IV) in a 1:1 isomer ratio based on nmr analysis of the products. Glpc analysis of the product gave only one broad peak with a shoulder indicating that two isomers were present. The results are in contradiction to the reported[6] results of earlier workers, who found only IV. In the present case these



$$(CH_3O)_2\overset{\overset{O}{\|}}{P}S\overset{\overset{CH_3}{|}}{C}HCH_2Cl$$

III

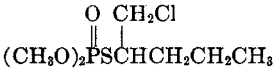


$$(CH_3O)_2\overset{\overset{O}{\|}}{P}SCH_2\overset{\overset{Cl}{|}}{C}HCH_3$$

IV

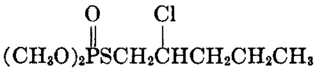
isomers were identified by their characteristics nmr spectra. Compound III shows its methylene protons as a doublet ($\delta = 3.77$ ppm), its methine proton as a multiplet at *ca.* 3.6 ppm, and its methyl protons as a doublet at 1.47 ppm. Compound IV exhibits its methylene protons as a doublet of a doublet at 3.10 ppm owing to the coupling with phosphorus and the adjacent methine proton. Its methine proton appears as a triplet of a quartet at 4.21 ppm and its methyl protons give rise to a doublet at 1.58 ppm.

Pentene-1.—The reaction of pentene-1 with I gave O,O′-dimethyl 2-S-1-chloropentylthiophosphate (V) and O,O′-dimethyl S-2-chloropentylthiophosphate (VI) in a 2:1 isomer ratio based on nmr analysis of the product mixture. These isomers could not be separated by glpc under a variety of conditions.



$$(CH_3O)_2\overset{\overset{O}{\|}}{P}S\overset{\overset{CH_2Cl}{|}}{C}HCH_2CH_2CH_3$$

V

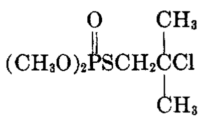


$$(CH_3O)_2\overset{\overset{O}{\|}}{P}SCH_2\overset{\overset{Cl}{|}}{C}HCH_2CH_2CH_3$$

VI

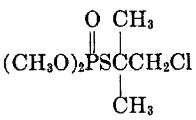
The methylene protons adjacent to chlorine in V appear as a doublet at 3.75 ppm. At 1.69 ppm, the multiplet for the C_3 and C_4 protons appears and the methyl protons of C_5 show up as a broad triplet at 0.98 ppm. The spectrum of VI shows the methine proton as a quintet at 3.98 ppm and the methylene protons adjacent to sulfur as a doublet of a doublet ($\delta = 3.13$ ppm) owing to the additional coupling with the phosphorus nucleus. The remaining protons give signals coincident with similar protons of the other isomer.

Isobutylene.—The reaction product of I with isobutylene contains three major components. All of these have been positively identified by a study of their nmr and infrared spectra. The product mixture consists of O,O′-dimethyl S-2-methyl-2-chloropropylthiophosphate (VII, 57%), O,O-dimethyl 2-S-(2-methyl-1-chloro)propylthiophosphate (VIII, 19%), and O,O′-dimethyl S-2-methallylthiophosphate (IX, 24%) based on nmr and glpc analysis of the products. A fourth



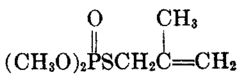
$$(CH_3O)_2\overset{\overset{O}{\|}}{P}SCH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}Cl$$

VII



$$(CH_3O)_2\overset{\overset{O}{\|}}{P}S\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_2Cl$$

VIII



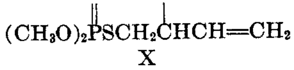
$$(CH_3O)_2\overset{\overset{O}{\|}}{P}SCH_2\overset{\overset{CH_3}{|}}{C}{=}CH_2$$

IX

component in the crude product (6%) remains unidentified. Again, these results differ from those reported by earlier workers[6] who found only VII. Compound VII's methylene protons appear as a doublet at 3.25 ppm owing to phosphorus coupling; the singlet at 1.66 ppm was attributed to the six equivalent methyl protons. The infrared spectrum of a mixture of VII and VIII proved to be consistent with the assigned structures, showing bands at 2850 cm^{-1} (OCH_3, CH stretching),[10b] 1385 and 1369 cm^{-1} (*gem*-dimethyl),[10c] 825–700 cm^{-1} (CCl stretching).[10d] The nmr spectrum of VIII shows the methylene proton singlet at 3.91ppm and a doublet at 1.55 ppm for the methyl protons split by long coupling with the phosphorus nucleus ($J = 1.5$ cps). The multiplets at 5.02 and 4.88 ppm in IX's nmr spectrum were assigned to the two nonequivalent terminal methylene protons. The broad doublet at 3.44 ppm was assigned to the methylene protons adjacent to the sulfur, split by the phosphorus, and the expected methyl proton multiplet appears at 1.86 ppm. An infrared spectrum of the compound confirms the proposed structure for IX, having bands at 3080 ($=CH_2$ stretching[10e]), 1805 ($=CH_2$ overtone of out-of-plane hydrogen deformation[10f]), 1645 (C=C stretching[10g]), and 900 cm^{-1} ($R_2C{=}CH_2$, out-of-plane hydrogen deformation[10f]).

Compound IX was also identified in the crude reaction product and, therefore, is not a product of any decomposition during distillation.

1,3-Butadiene.—The reaction of I with butadiene gave exclusively 1,2 addition, yielding a product mixture consisting of O,O′-dimethyl S-(2-chloro-3-butenyl)-thiophosphate (X) and O,O′-dimethyl 2-S-(1-chloro-3-butenyl)thiophosphate (XI) in an isomer ratio 73:27, respectively, based on nmr analysis of the products. All attempts at glpc analysis of the products resulted in decomposition of the adducts on the column. Nmr



$$(CH_3O)_2\overset{\overset{O}{\|}}{P}SCH_2\overset{\overset{Cl}{|}}{C}HCH{=}CH_2$$

X

$$(CH_3O)_2\overset{\overset{O}{\|}}{P}S\overset{\overset{CH_2Cl}{|}}{C}HCH{=}CH_2$$

XI

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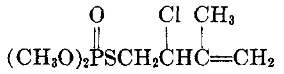
(10) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959: (a) p 312, (b) p 14, (c) p 24, (d) p 330, (e) p 43, (f) p 51, (g) p 35, (h) p 49, (i) p 53, (j) p 44, (k) p 36.

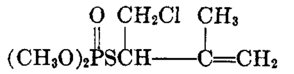
and infrared analyses of the products afforded their structure. The doublet of a doublet at 3.19 ppm, in the spectrum of X was assigned to the α-methylene protons split by coupling with the adjacent methine proton and the phosphorus nucleus. The methine proton appears as a quartet at 4.58 ppm. The vinylic proton appears as a multiplet at *ca.* 5.8 ppm. The pair of terminal vinylic protons appears as a multiplet at *ca.* 5.4 ppm. Compound XI's nmr spectrum coincides with that of X except for a doublet owing to the methylene protons adjacent to chlorine at 3.79 ppm and the multiplet at *ca.* 3.9 ppm attributed to the compound's methine proton α to sulfur. An infrared spectrum confirms the 1,2 nature of the adducts as shown by the bands at 3080 (=CH— stretching[10e]), 2995 (=CH_2 stretching[10e]), 1637 ($RCH{=}CH_2$, C=C stretching[10g]), and 930 cm^{-1} (=CH_2, out-of-plane deformation[10h]). The band for the =CH— out-of-plane deformation is a shoulder (*ca.* 995 cm^{-1}) on the very strong P—O band. No evidence for the 1,4-addition product was found in the nmr or infrared spectra.

A recent paper on the addition of O,O′-diethylphosphorylsulfenyl chloride to butadiene reported structure X as the only adduct.[9]

Isoprene.—The addition of I to isoprene gave a mixture of O,O′-dimethyl S-(3-methyl-2-chloro-3-butenyl)-thiophosphate (XII) and O,O′-dimethyl 2-S-(3-methyl-1-chloro-3-butenyl)thiophosphate (XIII). The isomer ratio of XII:XIII (65:35) was determined by nmr analysis, since the products could not be eluted from the chromatographic column.


$(CH_3O)_2\overset{O}{\overset{\|}{P}}SCH_2\overset{Cl}{\overset{|}{C}}H\overset{CH_3}{\overset{|}{C}}{=}CH_2$

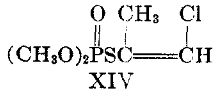
XII


$(CH_3O)_2\overset{O}{\overset{\|}{P}}S\overset{CH_2Cl}{\overset{|}{C}}H{—}\overset{CH_3}{\overset{|}{C}}{=}CH_2$

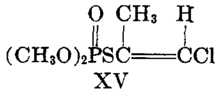
XIII

The nmr of XII shows a doublet of a doublet at 3.18 ppm which was assigned to the C_1 protons coupled to the adjacent proton and phosphorus. The methine proton was assigned to the broad triplet at 4.59 ppm; the methyl protons appear as a multiplet at 1.82 ppm. The two nonequivalent terminal methylene protons account for the pair of quartets at 5.03 and 5.13 ppm. The infrared spectrum shows peaks at 3080 (=CH_2 stretching[10e]), 1645 (C=C stretching[10g]), 1415 (=CH_2 in-plane hydrogen deformation[10i]), and 905 cm^{-1} (=CH_2 out-of-plane hydrogen deformation) confirming the indicated addition structures. The 2,1-addition product XIII also had characteristic nmr and infrared spectra. The methylene group adjacent to the chlorine appears as a triplet at 4.01 ppm. Its multiplicity must be due to equal coupling with both the methine proton and the phosphorus nucleus ($J_{PSCCH} = J_{HCCH}$ 6.7 cps). The signal of the methine proton is shifted downfield due to its allylic nature and, therefore, is coincident with the methoxy protons. The other protons in the molecule are coincident with those of the major isomer.

Methylacetylene.—Treatment of methylacetylene with I produced a mixture of *trans*- and *cis*-O,O′-dimethyl 2-S-(1-chloropropenyl)thiophosphate. These isomers, XIV (71%) and XV (29%, based on nmr and glpc analysis), were identified by careful study of the nmr and infrared spectra of the crude product mixture. The nmr spectra of XIV and XV show long-range coupling between phosphorus and the vinylic proton. The larger J value of 7.2 cps has been assigned to the isomer (XV) having the two groups *trans* in respect to the double bond. This isomer also shows the smaller (1.1 *vs.* 1.5 cps) coupling between the *cis*-methyl group and the olefin proton as expected. The vinylic proton of XIV appears as a quartet of a doublet at 6.54 ppm coupled both with the phosphorus by long-range interaction and with the methyl group's protons. The doublet of a doublet at 2.17 ppm is assigned to the methyl protons which are split by coupling to the vinylic proton and by long-range coupling with the phosphorus. The *cis* isomer XV shows its vinylic proton as a quartet of a doublet also, but this appears at 6.06 ppm. The methyl protons are again split into a doublet of a doublet with δ = 2.24 ppm. An infrared spectrum of the mixture has peaks at 3065 ($R_2C{=}CHR$, CH stretching[10j]) and 1610 cm^{-1} (C=C stretching[10k]) which help confirm the product's structures.


$(CH_3O)_2\overset{O}{\overset{\|}{P}}S\overset{CH_3}{\overset{|}{C}}{=\!=}\overset{Cl}{\overset{|}{C}}H$

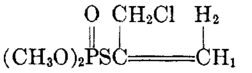
XIV


$(CH_3O)_2\overset{O}{\overset{\|}{P}}S\overset{CH_3}{\overset{|}{C}}{=\!=}\overset{H}{\overset{|}{C}}Cl$

XV

Since these isomers were separated fairly well by glpc, they were analyzed by the combined technique of gas chromatography and time-of-flight mass spectrometry. The two isomers gave exactly the same fragmentation patterns (Table IV) as would be expected of *cis–trans* isomers. No evidence for the reverse addition product was found.

Allene.—Reaction of I with allene gave O,O′-dimethyl 2-S-3-chloropropenylthiophosphate (XVI) identified by study of its nmr and infrared spectra. In this case, we are in agreement with the mode of addition reported for the corresponding O,O′-diethylphosphorylsulfenyl chloride.[8]


$(CH_3O)_2\overset{O}{\overset{\|}{P}}S\overset{CH_2Cl}{\overset{|}{C}}{=\!=}\overset{H_2}{\overset{|}{C}}H_1$

XVI

The triplet of a doublet at 5.98 ppm in the nmr spectrum of XVI was assigned to vinylic proton H_1 which is coupled long range to the allylic methylene protons and the phosphorus. Vinylic proton H_2 appears as a broad doublet at 5.77 ppm caused by long-range coupling to the phosphorus. The allylic protons were seen as a doublet of a doublet at 4.32 ppm owing to long-range coupling to both hydrogen and phosphorus. The infrared spectrum confirms the above structural assignment and shows peaks at 3090 (=CH_2 stretching[10f]), 930 (=CH_2 out-of-plane hydrogen deformation[10f]), and 680–825 cm^{-1} (CCl stretching [10d]). The nmr spectra did not rule out the presence or absence of the reverse addition product $(CH_3O)_2P(O)SCH_2C(Cl){=}CH_2$. The methylene protons adjacent to the sulfur would be expected to have a chemical shift similar to that of the methoxy protons and could be obscured by those signals. Similarly, the other protons in the molecule would be expected to be coincident with those of XVI. Glpc analysis showed a single, however, somewhat broad peak. The time-of-flight mass spectra taken at various points on the peak were identical (Table IV) suggesting that no significant amount of the reverse adduct was formed.

TABLE IV

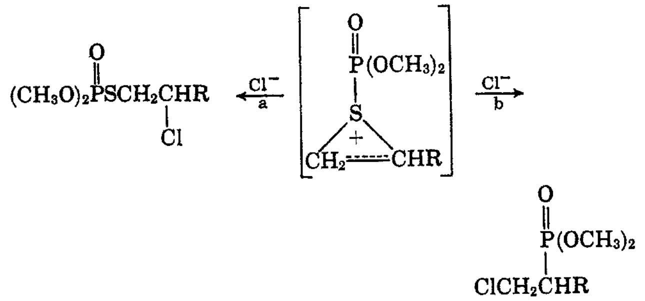
MAJOR MASS SPECTRAL FRAGMENTATION AND REARRANGEMENT IONS

cis- and *trans*-$(CH_3O)_2P(O)SC(CH_3){=}CHCl$		$(CH_3O)_2P(O)SC(CH_2Cl){=}CH_2$	
m/e	Structure	*m/e*	Structure
216	$[(CH_3O)_2P(O)SC(CH_3){=}CHCl]^+$	216	$[(CH_3O)_2P(O)SC(CH_2Cl){=}CH_2]^+$
181	$[(CH_3O)_2P(O)SC(CH_3){=}CH]^+$	181	$[(CH_3O)_2P(O)SC(CH_2){=}CH_2]^+$
142	$[(CH_3O)_2P(O)SH]^+$	142	$[(CH_3O)_2P(O)SH]^+$
125	[*m/e* 142 OH]	125	$[(CH_3O)_2P(S)]^+$
110	$[(CH_3O)_2POH]^+$		
109	$[(CH_3O)_2P{=}O]^+$	109	$[(CH_3O)_2P(O)]^+$
95	$[SPO_2]$		
		93	$[125 - 32]^+$ and $[109 - 16]^+$
79	$[CH_3OPOH]^+$	79	$[CH_3OPOH]^+$
72	[*m/e* 181 − 109]	72	$[181 - 109]^+$
		71	$[181 - 110]^+$
		49	$[CH_2Cl]^+$
47	$[PO]^+$	47	$[PO]^+$
40	$[C_3H_4]^+$		
39	$[C_3H_3]^+$	39	$[C_3H_3]^+$
35	$[Cl]^+$	35	$[Cl]^+$
15	$[CH_3]^+$	15	$[CH_3]^+$

Discussion

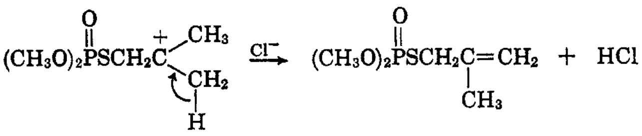
The generally accepted mechanism for the ionic addition of sulfenyl chlorides to double bonds involves the formation of an episulfoniun ion intermediate and subsequent ring opening on the most substituted carbon atom to yield predominantly Markovnikov-oriented adducts.[11]

The present study, however, demonstrates that the products from dialkylphosphorylsulfenyl chloride additions to terminal olefins cannot be predicted simply on the basis of the electronic effects underlying the Markovnikov rule (path a). Depending on the nature of the substituents on the double bond, the sterically controlled nucleophilic ring opening of the episulfonium ion intermediate by chloride ion may become an equally important, or even the predominant path "b" leading to anti-Markovnikov adducts, *e.g.*



Thus, with increasing size of the substituent "R" from methyl to propyl, path b becomes increasingly more important. If, however, the electronic nature of R can contribute significantly to the stabilization of a partial positive charge on the adjacent carbon of the intermediate, path a will be preferred. This becomes evident in the case of butadiene and isoprene. The selective attack on the less substituted double bond of isoprene, however, seems to indicate that steric effects cannot be eliminated.[12]

The accumulative effect of dialkyl substitution also appears to be sufficient to favor path a. This was demonstrated with isobutylene. Moreover, it seems that stabilization of the two substituents allows the formation of a true carbonium ion intermediate which would account readily for the observed isopropenylthiophosphate product.



We prefer this interpretation over the possibility of dehydrohalogenation taking place subsequent to adduct formation, since no such evidence was found during the more stringent conditions of work-up and distillation. In view of the above, the lack of 1,4 adducts from conjugated dienes is, however, surprising and requires a bridged intermediate.

The observed mixture of *cis* and *trans* adducts from methylacetylene may be due to postisomerization, since the product ratio changed slightly in repetitive experiments. The dependence of product orientation on solvent has recently been reported[13] and on the basis of kinetic evidence a complex mechanism for the addition of sulfenyl chlorides to triple bonds has been suggested.[14]

Experimental Section

Method of Analysis.—The adduct mixtures were analyzed by gas chromatography (gc) using an F and M Model 500, linear-programmed temperature gas chromatograph with a 3-ft, 0.25-in. o.d. column. The column packing consisted of 3% Dowfax 9N40 (an ethylene oxide–*p*-nonylphenyl polyether of a 40:1 molar ratio) on 60–80 mesh Gas Chrom P. Operating conditions were as follows: detector, 250°; injector, 140°; flow rate, 65 cc/min; column heating rate, 5.6°/min; starting temperature, 50°; final temperature, 245°; sample size, 1.0 μl.

Gas–liquid partition chromatography time-of-flight mass spectroscopy analysis[15] was obtained with a gas chromatograph (type, column, and conditions used were the same as above) ganged to a time-of-flight mass spectrometer. The effluent from the gas chromatograph was metered into the spectrometer through a connecting line and a metering valve (vari-vac Model VV-500C, manufactured by Vactronic Laboratory Equipment,

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(11) N. Kharasch, in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, Inc., New York, N. Y., 1961, p 382.

(12) Recent work in this laboratory showed that methanesulfenyl chloride or benzene-sulfenyl chloride addition to the less substituted double bond of 1,3-dienes is preferred: W. H. Mueller and P. E. Butler, to be published.

(13) V. Calo, G. Melloni, G. Modena, and G. Scorrano, *Tetrahedron Letters*, **49**, 4399 (1965), and references therein.

(14) L. DiNunno, G. Melloni, G. Modena, and G. Scorrano, *ibid.*, **49**, 4405 (1965).

(15) R. A. Brown and E. R. Quiran, *Appl. Spectry.*, **17**, 33 (1963).

Inc.) heated to 200°. The spectrometer was a Bendix Instrument, Type 12-101, which has been modified to include a 1.66-m flight tube, multigate recording, and improved electron-beam focusing. A multichannel Minneapolis–Honeywell Visicorder was used to record the mass spectral data obtained (Table IV).

Nuclear magnetic resonance (nmr) spectra were run on a Varian A-60 spectrometer as *ca.* 50% solutions in CCl_4 with tetramethylsilane as an internal standard unless stated otherwise.

Infrared spectra were recorded on a Beckman Model IR 10 infrared spectrophotometer.

Starting Materials. Unsaturates.—Ethylene (99.9% purity), propylene (99.7% purity), allene (+99% purity), methylacetylene (+98% purity), isobutylene (+99% purity), and 1,3-butadiene (+99% purity) were obtained from the Matheson Co. The pentene-1 used was a Phillips Chemical Co. product of +99% purity. The isoprene was distilled before use and was found to be pure by glpc analysis.

O,O′-Dimethyl Phosphorochloridothioate.—This reagent was obtained from the Monsanto Chemical Co. in +96% purity.

Preparation of Trimethyl Phosphorothionate.—An equimolar quantity of sodium methoxide dissolved in methanol was added slowly to O,O′-dimethyl phosphorochloridothioate with constant stirring. The reaction temperature was kept below 20°. The NaCl precipitate was filtered out of the solution and the methanol was removed on a rotary vacuum evaporator. The remaining liquid was distilled under reduced pressure affording the trimethyl phosphorothionate in *ca.* 70% yield, bp 77–80° (21 mm) [lit.[16] bp 82° (20 mm), 73% yield].

Preparation of O,O′-Dimethylphosphorylsulfenyl Chloride.—Sulfuryl chloride (54.0 g, 0.4 mole) was added dropwise to 62.5 g (0.4 mole) of trimethyl phosphorothionate. The temperature of the reaction was kept below 0° with an ice–salt bath. The reaction was stirred for 30 min after the addition was complete and then the gaseous products and unconsumed sulfuryl chloride were removed using a rotary vacuum evaporator followed by evacuation with an oil pump (1.0 mm). This afforded 64.9 g (92% yield) of the deep yellow $(CH_3O)_2P(O)SCl$, $n^{20}D$ 1.4818 (lit.[7] $n^{20}D$ 1.4820).

General Methods of Addition of O,O′-Dimethylphosphorylsulfenyl Chloride to Unsaturates. A. Liquid Unsaturates.—$(CH_3O)_2P(O)SCl$ was added dropwise to a 5 molar excess of the unsaturate contained in a three-neck flask fitted with a thermometer, a condenser with nitrogen purge, an addition funnel, and a magnetic stirrer. The reaction temperature was kept below 0° with an ice–salt bath. After the addition was complete the reaction mixture was brought slowly to room temperature. The excess olefin was removed under reduced pressure and the remaining oil was taken up in ether. The ethereal solution was washed with 5% $NaHCO_3$ solution until basic and then with water until neutral, and was dried over $MgSO_4$. Then the ether was removed under reduced pressure. The remaining oil (the "crude" product) was then distilled under high vacuum using an apparatus with a heated, packed column and a short-path condenser.

B. Gaseous Unsaturates.—Approximately 12 g of $(CH_3O)_2P(O)SCl$ was placed in a 25-ml, three-neck flask fitted with a thermometer, a condenser with nitrogen purge, and a gas inlet connected through a train of traps and bubblers to the olefin tank. The olefin was blown through the sulfenyl chloride at a moderate rate until the yellow color of the sulfenyl chloride either disappeared or remained constant. The temperature of the reaction was kept below 10° with an ice bath. The product was taken up in 50 ml of ether and was washed until basic with 5% $NaHCO_3$ solution. The ethereal solution was then washed with water until neutral and dried over $MgSO_4$. The ether was removed under reduced pressure and the remaining oil (the "crude" product) was distilled under high vacuum using a heated, packed column and a short-path condenser.

C. Gaseous Unsaturates.—Dried CH_2Cl_2 (100 ml) was placed in a 250-ml, four-neck flask fitted with a thermometer, a condenser with nitrogen purge, a dropping funnel with glass tubing extending below the surface of the methylene chloride. A 5 molar excess of the gaseous unsaturated (*ca.* 0.5 mole) was condensed into a graduated cylinder kept in a Dry Ice–isopropyl alcohol bath. Approximately 0.1 mole of $(CH_3O)_2P(O)SCl$ was added slowly to the unsaturated CH_2Cl_2 solution. The temperature was kept 10–15° below the boiling point of the unsaturated. After the addition was complete the reaction was allowed to come slowly to room temperature. The solution was washed until basic with a 5% solution of $NaHCO_3$, washed with water until neutral, and then dried over $MgSO_4$. The solvent was removed under reduced pressure and the remaining oil (the "crude" product) was distilled under high vacuum using a heated, packed column and a short-path condenser. In all cases the crude product was analyzed by glpc and nmr. Yields were calculated from the above analyses of the crude products (Table I). Decomposition during distillation diminished the yields. All distilled products were also analyzed by nmr and glpc and the nmr parameters of the products are tabulated in Tables II and III.

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[16] Reference 4, p 624.

Stereochemistry of Amine Additions to Acetylenic Sulfones and Carboxylic Esters[1]

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The reactions of amines with ethyl propiolate and several ethynyl sulfones have been studied. Dialkylamines react with these acetylenic compounds to give only *trans*-aminovinyl products. Ethylenimine reacts with both ethyl propiolate and 1-ethylsulfonyl-1-propyne to give mixtures of *cis* and *trans* products, with the relative ratios being solvent dependent, and with *p*-tolylsulfonylacetylene to give only *cis* product. Primary aliphatic amines react with both ethyl propiolate and 1-ethylsulfonyl-1-propyne to give mixtures of *cis* and *trans* products and with *p*-tolylsulfonylacetylene to give only *trans* products. Theories to explain all of these results are presented. In some of these systems the progress of the reactions was successfully followed by nuclear magnetic resonance.

Several years ago, during the course of work involving nucleophilic replacements of halogens from olefinic centers, a pronounced tendency was noted for base-induced additions of thiols to acetylenes to proceed in a *trans* manner.[2] This work, along with the accompanying theory and a few scattered indications in the literature of only one isomer being obtained in such nucleophilic additions, led to the postulation of "the rule of *trans*-nucleophilic addition." It next became of interest to study the applicability of this rule to additions involving nonanionic nucleophiles. The renewed and spreading interest in this area of chemistry[3,4] prompts us to report our observations on the stereochemistry of additions of several amines to acetylenic sulfones and carboxylic esters.

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[1] Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

[2] W. E. Truce and J. A. Simms, *J. Am. Chem. Soc.*, **78**, 2756 (1956).

[3] (a) J. E. Dolfini, *J. Org. Chem.*, **30**, 1298 (1965); (b) C. J. M. Stirling, *J. Chem. Soc.*, Suppl I, 5863 (1964).

[4] E. Winterfeldt and H. Preuss, *Angew. Chem.*, **77**, 679 (1965).