Alanine (680 mg, 76%) was obtained, $[\alpha]^{25}D$ −11.6° (*c* 3.75, 5 *N* HCl), 80% optically pure. The alanine was converted into DNP-alanine in the conventional manner,[11] and the resulting DNP derivative was purified by the use of a Celite column treated with pH 7.0 citrate buffer.[12] The DNP-alanine was extracted and crystallized: mp 170–173°; $[\alpha]^{25}D$ −120° (*c* 0.40, 1 *N* NaOH), 83% optically pure.

Optically active aspartic acids were prepared in the same way as above from oxaloacetic acid (reaction 26). The resulting aspartic acid and alanine were separated by the use of a Dowex 2-X8 column (formate form) by eluting with water. The aspartic acid combined with the resin was eluted with 1 *N* formic acid.

Other experimental procedures used in this study were similar to those which were reported already.[10]

Registry No.—(*S*)(+)-ala, 56-41-7; (*R*)(−)-ala, 338-69-2; (*S*)(+)-ala benzyl ester, 17831-01-5; (*R*)(−)-ala benzyl ester, 17831-02-6; (*S*)(+)-ph-gly, (*S*)(+)-asp, 56-84-8; (*R*)(−)-asp, 1783-96-6; (*S*)(+)-glu, 56-86-0; (*R*)(−)-glu, 6893-26-1.

Acknowledgment.—This work was supported by Grant No. NsG-689 of the National Aeronautics and Space Administration. The authors wish to express their thanks to Dr. Howard B. Powell and Dr. Cecil M. Criss for valuable discussion and to Mr. Charles R. Windsor for amino acid analysis.

Novel 1-Thiovinyl Phosphates and Related Materials

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Phosphites react with aryl and aralkyl chlorothiolacetates to give principally 1-thiovinyl phosphates; simple alkyl chlorothiolacetates give mixtures containing appreciable amounts of the isomeric phosphonates. Di- and trichlorothiolacetates give almost exclusively phosphates. Several of the phosphates were oxidized to the corresponding 1-sulfinyl and 1-sulfonylvinyl analogs. Proof of structure and mechanisms are given.

The literature on the reaction of halothiolacetates and trialkyl phosphites has been confusing. As early as 1951, S-ethyl,[1,2] S-carbethoxymethyl, S-phenyl, and other S-aryl trichlorothiolacetates[2] with triethyl phosphite were claimed to give phosphonates. Mel'nikov, *et al.*,[3,4] claimed the phosphonate structure for the products from ethyl, *p*-chlorophenyl, and 2,4,5-trichlorophenyl chlorothiolacetates similar to the products obtained from alkyl and aryl chloroacetates.[5] Patent literature[6−8] available after most of the work reported herein had been completed has disclosed 1-thiovinyl phosphates and the corresponding 1-sulfinylvinyl phosphates having only —C=CHCl and —C=C-Cl_2 groups. The —C=CCl_2 compounds might be expected since the structure of the reaction products obtained from trialkyl phosphites and trichloroacetates has been shown[9−11] to be that of the vinyl phosphate; however, the corresponding phosphonate structure from the trichloroacetates has also been indicated in some earlier literature.[12,13] More recently, Gololobov[14] reported a series of 1-thiovinyl phosphates obtained from S-ethyl mono-, di-, and trichlorothiolacetates and phosphites. Gololobov reported obtaining mixtures with the monochloro ester and only vinyl phosphates with the di- and trichloro esters.

(1) Ciba A.-G., Switzerland Patent 310,409 (1955).
(2) Farbenfabriken Bayer A.-G., German Patent Application F10,391 (120 23/03) (1955).
(3) N. N. Mel'nikov, *et al.*, USSR Patent 116,879 (1958).
(4) N. N. Mel'nikov, Ya. A. Mandel'baum, and V. I. Lomakina, *J. Gen. Chem. USSR* (Engl. Transl.), **29**, 3252 (1959).
(5) Ciba A.-G., Switzerland Patent 310,410 (1955).
(6) Sumitomo Chemical Industries Co., Ltd., Japan Patent Publication No. 4998 (1960).
(7) Sumitomo Chemical Industries Co., Ltd., Japan Patent Publication No. 13148 (1960); see also 17015 (1960).
(8) Sumitomo Chemical Industries Co., Ltd., Japan Patent Publication No. 16438 (1960).
(9) P. Mueller (to J. R. Giegy A.-G.), Switzerland Patent 326,948 (1958).
(10) Sumitomo Chemical Industries Co., Ltd., Japan Patent Publication No. 13147 (1960).
(11) F. W. Lichtenthaler, *Chem. Rev.*, **61**, 607 (1961).
(12) R. Sallmann (to Ciba Ltd.), U. S. Patent 2,830,927 (1958).
(13) R. Sallmann (to Ciba Ltd.), U. S. Patent 2,861,914 (1958).
(14) Yu. G. Gololobov, *J. Gen. Chem. USSR* (Engl. Transl.), **35**, 1246 (1965).

1-Thiovinyl Phosphates.—Our work independently showed that alkyl esters of monochlorothiolacetates gave mixtures while the corresponding aryl esters gave predominantly the 1-thiovinyl phosphates. All of the di- and trichloro esters used in this work gave the vinyl phosphates as the only detectable product.

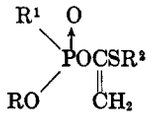
The S-substituted 1-thiovinyl phosphates,[15] yields, analyses, and properties are shown in Tables IA and IB. Yields in general were high. The phosphates generally are high-boiling liquids, not well purified by distillation. In one case where the thiovinyl phosphate (**1**) and the isomeric phosphonate were separated by distillation, the phosphonate was the higher boiling. Elemental analysis does not distinguish the 1-thiovinyl phosphates from the isomeric phosphonate; however, infrared spectra clearly established the 1-thiovinyl phosphate structure and were also used to detect the presence of phosphonate. Calibrated infrared spectra were not obtained, and a minimum of 5–10% of the phosphonate could probably be detected.

Proof of Structure.—It was noted early in this work that the infrared spectra did not confirm the phosphonate structure, primarily owing to the absence of a carbonyl band in the 5.5–6.0-μ region. The phosphate structure was assigned on the basis of the presence of a C=C band in the 6–6.2-μ region and a split P→O band characteristic of phosphates.[16]

The spectrum of **1**, like those of all of the 1-thiovinyl phosphates, had no C=O absorption at 5.89 μ which was present in the spectra of the phosphonates of this type. A moderately strong C=C absorption at 6.21 μ was present in **1** but absent in the phosphonates. Also, **1** had a split P→O absorption at 7.7 and 7.8 μ which is characteristic of a phosphate group, while the phosphonates had a single P→O absorption at 7.95 μ characteristic of a phosphonate grouping.[17]

(15) L. F. Ward, Jr., and D. D. Phillips (to Shell Chemical Co.), U. S. Patent 3,069,313 (1962).
(16) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956.
(17) F. S. Mortimer, *Spectrochim. Acta*, **9**, 270 (1957).

TABLE IA
STRUCTURE AND PROPERTIES OF 1-THIOVINYL PHOSPHATES UNSUBSTITUTED IN 2 POSITION

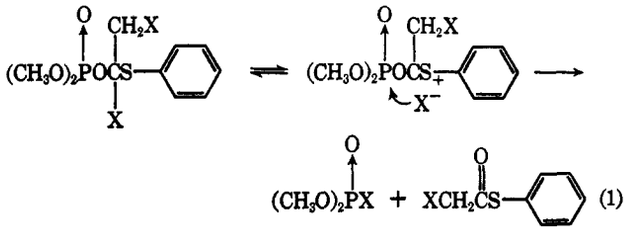


Compd	R	R^1	R^2	Yield, %	Bp, °C (mm)	$n^{25}D$	d (25°)		Anal., % Found	Anal., % Calcd	Hydrolysis, 38°, half-life, hr: pH 1.1[a]	Hydrolysis, 38°, half-life, hr: pH 9.1[b]
1	CH_3	CH_3O	CH_3	34	67–68 (<0.02)	1.4695	1.2	P	15.7	15.7	7	60
								S	16.4	16.2		
								Cl	<0.1	0.0		
2	CH_3	CH_3O	C_6H_5	68	95–98 (0.018)	1.5320	1.2	P	11.8	11.9	<7	170
								S	11.7	12.3		
								Cl	0.2	0.0		
3	CH_3	CH_3O	$2\text{-}C_{10}H_7$	75	145–150 (0.001)	1.6000	1.3	P	9.5	10.0	7	70
								S	10.7	10.3		
								Cl	0.46	0.0		
4	C_2H_5	C_6H_5	C_6H_5	72	145–150 (0.001)	1.5684	1.0	P	9.8	9.7	7	10
								S	10.1	10.0		
								Cl	0.26	0.0		
5	C_2H_5	C_2H_5O	C_6H_5	81	110–120 (0.001)	1.5182	1.1	P	10.8	10.8	<5	>100
								S	11.0	11.1		
								Cl	<0.1	0.0		
6	$i\text{-}C_3H_7$	$i\text{-}C_3H_7O$	C_6H_5	72	90 (0.001)	1.5032	1.1	P	9.6	9.8	9	120
								S	10.3	10.1		
								Cl	0.39	0.0		
7	C_4H_9	C_4H_9O	C_6H_5	80	125 (0.001)	1.5028	1.1	P	9.0	9.0	9	120
								S	9.0	9.3		
								Cl	0.35	0.0		
8	CH_3	CH_3O	$p\text{-}ClC_6H_4$	78	100–105 (0.001)	1.5442	1.3	P	10.6	10.5	<7	110
								Cl	12.3	12.1		
9	C_2H_5	C_2H_5O	$p\text{-}ClC_6H_4$	76	115 (0.001)	1.5302	1.2	P	9.1	9.6	<7	>300
								S	9.9	10.5		
10	CH_3	CH_3O	$Cl_3C_6H_2$	90	Crude	1.5610	1.5	P	8.5	8.5	24	35
								S	8.3	8.8		
								Cl	28.8	29.3		
11	C_2H_5	C_2H_5O	$Cl_3C_6H_2$	85	Crude	1.5568	1.4	P	7.1	7.9	14	115
								S	7.7	8.2		
								Cl	27.7	27.2		
12	CH_3	CH_3O	$p\text{-}NO_2C_6H_4$	76	Mp 70–71	...	...	P	10.3	10.2	24	75
								S	11.0	10.5		
								Cl	0.25	0.0		
13	CH_3	CH_3O	$p\text{-}CH_3C_6H_4$	71	118–122 (0.001)	1.5328	1.2	P	11.3	11.3	11	58
								S	11.8	11.6		
								Cl	0.4	0.0		
14	CH_3	CH_3O	$C_6H_5CH_2$	67	135–140 (0.001)	1.5295	1.2	P	11.8	11.3	12	35
								S	11.5	11.7		
								Cl	0.64	0.0		
15	C_2H_5	C_2H_5O	$C_6H_5CH_2$	68	125 (0.001)	1.5197	1.2	P	10.5	10.3	13	36
								S	10.8	10.6		
								Cl	0.27	0.0		

[a] 0.2–2.0 ppm in aqueous HCl. [b] 0.2–2.0 ppm in aqueous $K_2B_4O_7$.

With these exceptions and a band at 10.0–10.2 μ in the spectra of **1**, tentatively assigned to the C=CH_2 group, the spectra were otherwise very similar. The nmr spectra were also obtained for four 1-thiovinyl phosphates, and the nmr parameters are shown in Table II. These confirmed the presence of olefinic protons and absence of a saturated methylene group. In the case of **16** and **17** the presence of two doublets near 3.6 and 6.5 ppm indicated the presence of isomers around the double bond.

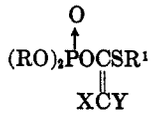
Halogenation of **2** and **5** afforded additional evidence of structure. Addition of 1 mol of chlorine (from sulfuryl chloride) to each of these materials gave the dichloroethyl phosphates. The infrared spectra of these two products no longer contained the C=C band at 6.2 μ. In addition, a band at about 10.2 μ present in all of the 1-thiovinyl phosphates containing either a C=CH_2 or C=CCl_2 grouping had been eliminated. Bromination of **2** also appeared to give the similar dibromoethyl phosphate. Both the chlorinated and brominated products decomposed to two immiscible materials shown by infrared spectra to be dimethyl halophosphate and S-phenyl halothiolacetate, presumably as shown in eq 1. Even though the halo-



(1)

TABLE IB

STRUCTURE AND PROPERTIES OF 1-THIOVINYL PHOSPHATES SUBSTITUTED IN 2 POSITION

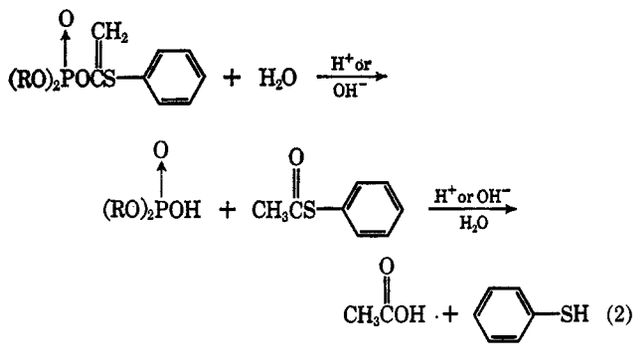


Compd	R	R¹	X	Y	Yield, %	Bp, °C (mm)	$n^{25}D$	d (25°)		Anal., % Found	Anal., % Calcd	Hydrolysis, 38°, half-life, hr: pH 1.1[a]	Hydrolysis, 38°, half-life, hr: pH 9.1[b]
16	CH_3	CH_3	H	Cl	90	80–81 (0.02)	1.4892	1.4	P	13.6	13.3	45	35
									S	13.9	13.8		
									Cl	15.4	15.3		
17	CH_3	C_6H_5	H	Cl	84	110 (0.001)	1.5468	1.3	P	10.6	10.5	120	28
									S	11.0	10.9		
									Cl	11.7	12.0		
18	C_2H_5	$C_6H_5CH_2$	H	Cl	65	125 (0.001)	1.5269	1.2	P	9.2	9.2		
									S	9.8	9.5		
									Cl	10.0	10.5		
19	C_2H_5	C_6H_5	Cl	Cl	77	110 (0.001)	1.5402	1.4	P	8.6	8.7	140	70
									S	8.7	9.0		
									Cl	20.1	19.9		
20	CH_3	C_6H_5	Cl	Cl	75	95 (0.001)	1.5565	1.4	P	9.3	9.4	77	14
									S	9.7	9.7		
									Cl	21.4	21.6		
21	CH_3	CH_3	Cl	Cl	87	94 (0.02)	1.5030	1.4	P	11.5	11.6	93	17
									S	12.0	12.0		
									Cl	26.5	26.6		
22	CH_3	C_6H_5	F	F	75	75–82 (0.001)	1.5023	1.3	P	10.9	10.5	170	13
									S	11.1	10.8		
									Cl	<0.1	0.0		

[a] 0.2–2.0 ppm in aqueous HCl. [b] 0.2–2.0 ppm in aqueous $K_2B_4O_7$.

genation was not a simple process, the intermediate and final products nevertheless substantiate the vinyl phosphate structure assigned.

Hydrolysis, described in more detail later, also afforded additional evidence of structure. In both acidic and basic solutions, the simple thiovinyl phosphates **2** and **5** hydrolyzed first at the POC bond followed by hydrolysis of the resultant thiolacetate (eq 2). This was demonstrated both by infrared spectra



(2)

and by glpc during the first 10–20% of hydrolysis in which essentially all of the material was present either as the 1-thiovinyl phosphate or as the thiolacetate. The thiolacetate was converted into benzenethiol during the later stages of hydrolysis.

Selectivity of Reaction.—Many variations were made both in substituents of the S-ester group as well as in the groups attached to phosphorus. The various changes affected the rate of reaction as followed by infrared spectroscopy. Conditions required for complete reaction varied from 1 hr at 60° to 14 hr at 110–130°. From the reaction times and temperatures, the following general conclusions concerning reactivity

TABLE II

NMR PARAMETERS

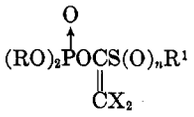
Compd	Group	Chemical shift δ, ppm	Coupling constant, Hz	Multiplicity	No. of protons
2	$-OCH_3$	3.6	$J = 11$	Doublet	6
	$=CH_2$	5.0	$J = 2$	Triplet	1
		5.32	$J = 2$	Triplet	1
	Aromatic	7.37			5
1	$-SCH_3$	2.31			3
	$-OCH_3$	3.82	$J = 11$	Doublet	6
	$=CH_2$	4.76	$J = 2$	Quartet	1
		5.10	$J = 2$	Quartet	1
16	$-SCH_3$	2.4			3
	$-OCH_3$	3.86, 3.87	$J = 11$	Two doublets	6
	$=CH-$	6.11	$J = 1$	Doublet	0.4
		6.38	$J = 3$	Doublet	0.6
17	$-OCH_3$	3.60, 3.67	$J = 11$	Two doublets	6
	$=CH-$	6.38	$J = 1.5$	Doublet	0.3
		6.6	$J = 3.0$	Doublet	0.7
	Aromatic	7.36			5

were drawn for the S-esters and phosphites reacted: (1) with S-phenyl chlorothiolacetate and different phosphites $C_6H_5P(OCH_3)_2 > (CH_3O)_3P > (C_2H_5O)_3P \cong (CH_3O)_2PN(CH_3)_2 > (i\text{-}C_3H_7O)_3P \cong (n\text{-}C_4H_9O)_3P \gg (CH_3O)_2POC_6H_5$: (2) with trimethyl phosphite and with variation in the R group of $ClCH_2C{=}OSR$ (a) $p\text{-}NO_2C_6H_4 > C_6H_5 \cong p\text{-}ClC_6H_4 \cong 2,4,5\text{-}Cl_3C_6H_2 > p\text{-}t\text{-}C_4H_9C_6H_4 > p\text{-}CH_3C_6H_4 \gg o\text{-}CH_3C_6H_4$, (b) $C_6H_5 > 2\text{-}C_{10}H_7 > C_6H_5CH_2 \gg C_6H_5CHCH_3$, (c) $C_6H_5CH_2 \gg CH_3OC{=}OCH_2 \gg CH_3$.

S-Aryl Analogs.—S-Aryl monochloro-, dichloro-, and trichlorothiolacetates were all found to yield only the corresponding S-substituted 1-thiovinyl phosphates as detected by infrared spectroscopy. This is in direct contrast to the product obtained from

TABLE III

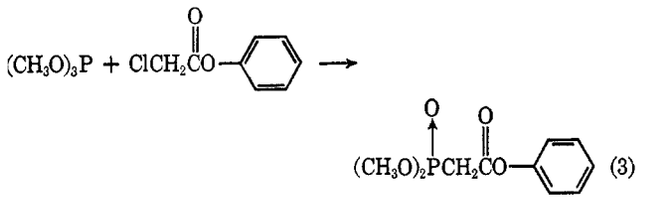
STRUCTURE AND PROPERTIES OF 1-SULFINYLVINYL AND 1-SULFONYLVINYL PHOSPHATES



Compd	R	R¹	X	n	Precursor (1-thiovinyl phosphate)	Yield, %	Bp, °C (mm)	$n^{25}D$	d (25°)		Anal., % Found	Anal., % Calcd	Hydrolysis, 38°, half-life, hr pH 1.1[c]	Hydrolysis, 38°, half-life, hr pH 9.1[d]
23	C_2H_5	C_6H_5	H	1	5[a]	69	115–120 (0.008)	1.5173	1.25	P	10.5	10.2	100	14
										S	10.5	10.5		
24	CH_3	*p*-ClC_6H_4	H	1	8[a]	44	120 (0.001)	1.5431	1.4	P	10.0	10.0	29	9
										S	10.8	10.3		
25	C_2H_5	$C_6H_5CH_2$	H	1	15[a]	66	125 (0.001)	1.5205	1.22	P	9.9	9.8	170	12
										S	10.2	10.1		
26	CH_3	CH_3	H	1	1[a]	51	75–80 (0.001)	1.4709	1.28	P	14.6	14.5	26	<7
										S	15.4	15.0		
27	C_2H_5	C_6H_5	H	2	5[b]	66	130–135 (0.009)	1.5045	1.25	P	9.8	9.7	40	8
										S	10.6	10.0		
28	CH_3	*p*-ClC_6H_4	H	2	8[b]	53	128 (0.001)	1.5321	1.4	P	9.2	9.5	17	<7
										S	10.3	9.8		
29	C_2H_5	*p*-ClC_6H_4	H	2	9[a]	68	125–130 (0.008)	1.5140	1.3	P	9.0	8.7	13	<7
										S	9.3	9.0		
30	CH_3	$Cl_3C_6H_2$	H	2	10[b]	79	Crude	1.5560	...	P	7.8	7.9	30	<8
										S	7.8	8.1		
31	C_2H_5	$C_6H_5CH_2$	H	2	15[a]	61	120–125 (0.001)	1.5082	1.24	P	9.3	9.3	46	<7
										S	9.9	9.6		
32	CH_3	CH_3	H	2	1[a]	80	Crude	1.4545	...	P	13.6	13.5	13	<7
										S	13.7	13.9		
33	C_2H_5	C_6H_5	Cl	2	19[b]	92	Crude	1.5322	...	P	7.8	8.0	...	...
										S	7.9	8.2		

[a] Peracetic acid used as oxidizing agent. [b] Monoperphthalic acid used as oxidizing agent. [c] 0.2–2.0 ppm in aqueous HCl. [d] 0.2–2.0 ppm in aqueous $K_2B_4O_7$.

phenyl chloroacetate (eq 3) which was only the phosphonate shown by the absence of any bands in the C=C region of the infrared spectra.



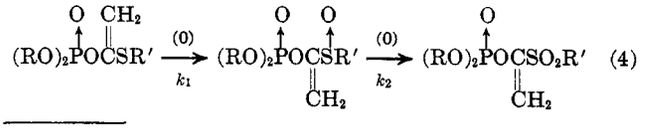
(3)

S-Aralkyl Analogs.—Aralkyl esters, *i.e.*, S-benzyl chlorothiolacetate, like the aryl analogs, also normally gave thiovinyl phosphates. These thiolacetates were in general less reactive than the S-phenyl materials, but gave the same high yields. However, the S-*p*-methylbenzyl and S-α-methylbenzyl chlorothiolacetates reacted with trimethyl phosphite very slowly, and both products contained some inseparable isomeric phosphonate. These exceptions might indicate that more of the 1-thiovinyl phosphates contain small amounts of the isomeric phosphonates, not detected with the methods used.

S-Alkyl Analogs.—All of the simple S-alkyl chlorothiolacetates gave mixtures of phosphates and phosphonates. The S-methyl ester gave about a 1:1 ratio of the 1-thiovinyl phosphate **1** (Table IA) and phosphonate. These two materials were separated by distillation, with the phosphate being the lower boiling component. Infrared spectrum of the mixture from the S-butyl ester indicated a predominance of phosphate. In contrast, although infrared spectroscopy indicated the presence of phosphate during the reaction, the S-allyl ester gave the phosphonate as the only isolable material. The methoxycarbonyl group when substituted on the methyl group of methyl chlorothiolacetate acted much like the phenyl portion of the benzyl group, discussed above, in that the vinyl phosphate was obtained in high yield. A consequence of this observation is discussed in the section devoted to the mechanism of the reaction.

The dichloro- and trichlorothiolacetates with S-alkyl ester groups reacted similarly to the corresponding S-aryl and S-aralkyl esters; *e.g.*, only 1-thiovinyl phosphates were detected or isolated. The S-alkyl dichloro- and trichlorothiolacetates had about the same reactivity requiring about 1 hr at 100°, whereas the corresponding monochloro derivatives were much less reactive requiring 13–14 hr at 100° for complete reaction.

Other Chemistry of 1-Thiovinyl Phosphates. Oxidation.—Several of the 1-thiovinyl phosphates were oxidized to the corresponding sulfoxides and sulfones.[18] These compounds and their properties are shown in Table III. The reaction with 2 equiv of oxidant apparently went stepwise *via* the sulfoxide. This was evidenced by the absence of the sulfone (SO_2) bands (7.4, 8.7 μ) in the infrared spectra of products obtained when exactly 1 equiv of oxidant was used. Thus, k_1 must be many times faster than k_2 (eq 4).



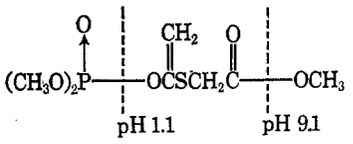
(4)

(18) D. D. Phillips and L. F. Ward, Jr. (to Shell Chemical Co.), U. S. Patent 3,151,147 (1964).

Hydrolysis.—The hydrolysis studies of the vinyl phosphates and related materials were carried out on aqueous solutions containing 0.2–2.0 ppm of the phosphate, using HCl for pH 1.1 and potassium tetraborate buffer for pH 9.1. In general, diethyl phosphates were more stable than the corresponding dimethyl compounds. Under strongly acidic conditions, hydrolysis was extremely rapid, especially with phosphates containing the $C{=}CH_2$ grouping, and very little difference in stability of ethyl–methyl pairs was noted.

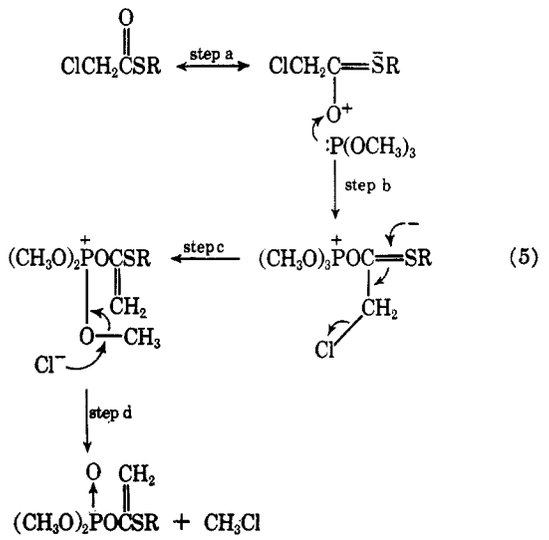
Except for the 1-thiovinyl phenylphosphonate (**4**) and the methoxycarbonylmethyl compound shown below, all of the phosphates containing an unoxidized sulfur (CSR′) and an unsubstituted α-methylene group ($C{=}CH_2$) were much less stable at pH 1.1 than at 9.1. This could be expected in view of their resemblance to acetals. However, when one of the α-methylene hydrogens was replaced by a methyl group, the stability at the two pH's was about the same. When one or both hydrogens were replaced by chlorine, the stability picture was reversed, and these halogenated derivatives were more stable at pH 1.1 than at pH 9.1. In general, the dichloro compounds were less stable than the corresponding monochloro analogs. Oxidation of the sulfur either to sulfoxide or sulfone also resulted in greater stability in acid solution, with the sulfoxide being the most stable. These results were expected owing to an inductive effect caused by the electron-withdrawing power of halogens and sulfoxide or sulfone groups which would tend to make the displaced anion and subsequent alcohol more stable as noted by Vernon.[19] There was no obvious reason for the instability of **4** in base, but the electron-attracting character of the benzene ring might make the P—O—C=C bond more susceptible to attack by bases.

In the case of the methoxycarbonylmethyl compound, an additional site is provided for hydrolysis. Carboxylic esters are rapidly hydrolyzed in base.[16] Consequently, under basic conditions, the hydrolysis of the $O{=}COCH_3$ group was probably the rate-determining step, whereas in acid the hydrolysis of the $POC{=}C$ bond determined the rate as shown. Hydrolysis of one or both of the methyl ester groups on phosphorus was also possible. However, as discussed earlier, only starting phosphate and thiolacetate were detected in the early stages of hydrolysis.



Mechanism of Reaction.—The mechanism of the reaction of trialkyl phosphites with α-halocarbonyl compounds to give vinyl phosphates has not been established. Attack of the carbonyl carbon by phosphorus followed by intramolecular rearrangement has been proposed to be the most likely mechanism with attack at the carbonyl oxygen less likely.[11,20,21] With halothiolacetates, however, attack on the carbonyl oxygen is most likely.

This mechanism involves the ability of the sulfur atom to expand its outer valence shell to ten electrons by use of the d orbitals, thus making the carbonyl oxygen somewhat positive (eq 5, step a). The electron-withdrawing character of the SR group is demonstrated by the infrared studies of Baker and Harris[22] who show that in thiolacetates, $O^+{=}C{=}{}^-SR$ is present. This electron-withdrawing character of the SR groups is also evidenced by the contrasting reactions of ethynyl ethers and thio ethers with nucleophilic reagents.[23] It will be noted that reaction of the unpaired electrons of trimethyl phosphite with the positive oxygen (step b) can give the phosphate bond directly; then the normal bond shifts (steps c and d) produce the 1-thiovinyl phosphate. The type of resonance depicted in step a becomes especially attractive when there is attached to sulfur a group which acts as an electron sink such as phenyl and substituted phenyl groups. This allows the negative charge to be delocalized to a greater extent and thus stabilizes the resonance hybrid.



(5)

The chemistry discussed earlier lends support to this mechanism. Attack on carbonyl oxygen can account for the formation of the vinyl phosphate from S-alkyl chlorothiolacetates. Simple alkyl groups are not electron sinks; in fact, they are somewhat electron donating.[24] However, the electron-withdrawing capacity of the sulfur apparently is still strong enough to produce some positive charge on the carbonyl oxygen. Thus, the reaction proceeds partly by this path when R is methyl and almost completely by step a when R is aryl.

The structural effect on reactivity of the aryl and aralkyl chlorothiolacetates mentioned earlier also lends support for attack on oxygen. Thus, substitution in the *para* position with a very strong electron-withdrawing group such as nitro increases the reactivity whereas substitution with electron-donating groups such as methyl or *t*-butyl decreases the reactivity.

In addition to the electron-attracting properties of the sulfur, one must consider the inductive effect of the

(19) C. A. Vernon, "Phosphoric Esters and Related Compounds," Special Publication No. 8, The Chemical Society, London, 1957, p 31.

(20) E. L. Gefter, "Organophosphorus Monomers and Polymers," Associated Technical Services Inc., Glen Ridge, N. J., 1962, pp 31–36.

(21) B. Miller, "Topics in Phosphorus Chemistry," Vol. 2, Interscience Publishers, New York, N. Y., 1965.

(22) A. W. Baker and G. H. Harris, *J. Amer. Chem. Soc.*, **82**, 1923 (1960).

(23) B. A. Raphael, E. C. Taylor, and H. Wynberg, *Advan. Org. Chem.*, **2**, 151 (1960).

(24) A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1947, p 149.

halogens. Additional chlorines as in di- and trichlorothiolacetates cause the carbonyl oxygen to become even more positive and account for the increased rates of reaction noted. Even when R is methyl, only two chlorines are required to shift product formation entirely over to the vinyl phosphate **16**.

Thus, based on the chemistry above and the work reported on thio esters,[22,23] attack on oxygen appears to be the most reasonable mechanism for thiolacetates.

Experimental Section

Instruments.—The infrared spectra were obtained on a Beckman IR-4 spectrophotometer, using carbon disulfide or methylene chloride as solvent and a 0.1-mm sodium chloride cell. Certain spectra were obtained with a Beckman IR-5 spectrophotometer. The nmr spectra were obtained in a Varian A-60 instrument with tetramethylsilane as internal reference standard. Chemical shifts are reported in parts per million (δ) from tetramethylsilane and coupling constants are reported in cycles per second (cps).

Preparation of Chlorothiolacetates.—All of the chlorothiolacetates used in the preparation of the thiovinyl phosphates and related materials were made from the appropriate thiols and haloacetyl chlorides following the procedure described by Dalgleish and Mann.[25] Yields generally were in excess of 70%.

Preparation of 1-Thiovinyl Phosphates and Isomeric Materials.—Two examples are given: (1) a preparation which gave vinyl phosphate cleanly, and (2) a preparation from which both 1-thiovinyl phosphate and the isomeric phosphonate were isolated.

Diethyl 1-(Phenylthio)vinyl Phosphate (5).—To S-phenyl chlorothiolacetate (259 g, 1.39 mol) at 90–100° was added triethyl phosphite (266 g, 1.60 mol), heated for a total of 4.5 hr at 110–120° and stripped to 125° (0.05 mm) (kettle temperature) to remove lower boiling materials. Molecular distillation of the residue gave an 81% yield of **5** as a pale yellow liquid: boiling range 110–120° (0.001 mm); $n^{25}D$ 1.5182; ir 3.23 (=CH), 6.2 (C=C), 7.62, 7.7 (P→O) (phosphate), 10.1 μ (C=CH_2).

Anal. Calcd for $PSO_4C_{12}H_{17}$: P, 10.8; S, 11.1; Cl, 0.0. Found: P, 10.8; S, 11.0; Cl, <0.1.

Dimethyl 1-(Methylthio)vinyl Phosphate (1) and S-Methyl (Dimethoxyphosphinyl)thioacetate.—Trimethyl phosphite (97% pure) (119 g, 0.92 mol of 100% purity) was added over 1 hr to the chloro ester (100 g, 0.80 mol) at 90–95°. The mixture was then heated for 13.5 hr at 90–115°, checking by infrared spectroscopy periodically to determine the extent of reaction. The mixture was then Claisen distilled to give two main fractions: (1) 58 g; bp 76–78° (0.02 mm); infrared, strong C=C, weak C=O, (2) 31 g; bp 95–105° (0.02 mm); infrared, very weak C=C, very strong C=O. Redistillation of fraction 1 through an 8-in. Bantam-ware unpacked column gave 41 g (26% yield) of **1** as a yellow liquid: bp 73° (0.02 mm); $n^{25}D$ 1.4710. Fraction 2, above, gave 31 g (20% yield) of the isomeric phosphonate, a yellow liquid, which was not further purified: bp 95–105° (0.02 mm); $n^{25}D$ 1.4770. Infrared analysis indicated that little if any phosphonate was present in **1**.

Anal. Calcd for $PSO_4C_5H_{11}$: P, 15.7; S, 16.2; Cl, 0.0. Found for **1**: P, 16.0; S, 15.5; Cl, 0.2. Found for crude phosphonate: P, 16.6; S, 13.6; Cl, 0.5.

Phenyl (Dimethoxyphosphinyl)acetate.—Trimethyl phosphite (27.5 g, 0.22 mol) was added to phenyl chloroacetate (34 g, 0.20 mol) at 35°. The resultant mixture was heated over 1.25 hr to a kettle temperature of 140°. Heating was continued for an additional 7 hr at 115–140°. The crude product was stripped at 95° (0.001 mm) and molecularly distilled at 105–110° (0.001 mm) to give 28 g (58% yield) of the phosphonate: $n^{25}D$ 1.5011; ir 3.50 (O—CH_3), 5.65 (C=O), 7.82 (P→O) (phosphonate), 9.6 μ (P—O—C). The infrared spectra of samples taken during the reaction and also prior to stripping showed no vinyl phosphate formation as evidenced by the absence of bands in the 6.0–6.2-μ region.

Anal. Calcd for $PO_3C_{10}H_{13}$: P, 12.7; Cl, 0.0. Found: P, 12.6; Cl, 0.5.

Diethyl 1-(Phenylsulfinyl)vinyl Phosphate (23).—To the 1-thiovinyl phosphate **5** (57.6 g, 0.20 mol) in 150 ml of chloroform was added 136 ml of a solution of peracetic acid in chloroform (15.9 g, 0.21 mol) over a 2.25-hr period at 20–30° with ice-bath cooling as needed. The mixture was stirred for an additional 1 hr at 25–30° when titration indicated only the excess (0.7 g) of peracetic acid remained. The solution was washed with cold aqueous 10% sodium bicarbonate solution until the washings were slightly basic to pH paper, separated, dried with magnesium sulfate, and stripped to remove solvent. The residual liquid was stripped and molecular distillation gave 42 g (69% yield) of **23** as a yellow liquid: bp 115–120° (0.008 mm); $n^{25}D$ 1.5173; infrared spectrum, similar to **5** except bands at 8.4, 9.15, and 9.45 μ, new or stronger; S→O near normal with smaller band near 8.5 μ.

Anal. Calcd for $PSO_5C_{12}H_{17}$: P, 10.2; S, 10.5. Found: P, 10.5; S, 10.5.

Dimethyl 1-(Methylsulfonyl)vinyl Phosphate (32). Method 1. Monoperphathalic Acid.—To the phosphate **1** (4.95 g, 0.025 mol) in 30 ml of ether was added 156 ml of an ethereal solution of monoperphthalic acid (9.55 g, 0.053 mol). The temperature rose spontaneously to 35°. The mixture was refluxed for 1 hr when titration showed 0.08 g of per acid remaining. The solution was filtered and washed with a 5% aqueous sodium bicarbonate solution until washings were basic to pH paper. The washings were saturated with sodium chloride and extracted five times with 50 ml of methylene chloride each. The ether and methylene chloride solutions were combined, and the total was dried with magnesium sulfate. The solvent was removed, and the residual liquid was stripped to a final temperature of 50° (0.2 mm) to give 4.5 g (80% yield) of **32** as a yellow liquid: $n^{25}D$ 1.4545; infrared spectrum, some changes from **1**, with the most prominent being the SO_2 bands at 7.5 and 8.8 μ.

Anal. Calcd for $PSO_6C_5H_{11}$: P, 13.5; S, 13.9. Found: P, 13.6; S, 13.7.

Method 2. Peracetic Acid.—To **1** (45.5 g, 0.23 mol) in 20 ml of chloroform was added 385 ml of a solution of peracetic acid (41 g, 0.54 mol) in chloroform, and the temperature was maintained at 25–35° by ice-bath cooling as needed. The mixture was stirred for an additional 1.5 hr at 25–30° when titration showed only the excess (6.2 g) per acid remained. Work-up similar to method 1 and molecular distillation gave 32 g (60% yield) of **32** as a very pale yellow liquid: bp 85° (0.002 mm); $n^{25}D$ 1.4552; infrared spectrum, similar to that in method 1 above, 7.49 and 8.78 μ for SO_2 bands.

Anal. Calcd for $PSO_6C_5H_{11}$: P, 13.5; S, 13.9. Found: P, 13.8; S, 14.1.

1,3-Dichloro-2-(phenylthio)ethyl Diethyl Phosphate.—To the phosphate **5** (10.3 g, 0.036 mol) in 25 ml of methylene chloride cooled to 5° was added sulfuryl chloride (4.7 g, 0.035 mol) in 10 ml of methylene chloride. The temperature was maintained at 5–10° by use of a Dry Ice–acetone bath as needed. The resultant solution was warmed to ambient temperature over a period of 30 min and then stripped at 25° (1.0 mm) for 2 hr to give 12.6 g (99% yield) of 1,2-dichloro-2-(phenylthio)ethyl diethyl phosphate as a yellow oil: $n^{25}D$ 1.5196.

Anal. Calcd for $PSO_4Cl_2C_{12}H_{17}$: P, 8.6; S, 8.9; Cl, 19.8. Found: P, 8.5; S, 9.1; Cl, 19.8.

Registry No.—**1**, 17604-41-0; **2**, 17604-42-1; **3**, 17604-43-2; **4**, 3661-33-4; **5**, 2274-95-5; **6**, 17604-46-5; **7**, 3661-28-7; **8**, 2595-53-1; **9**, 3842-84-0; **12**, 17604-50-1; **13**, 17604-51-2; **14**, 17604-52-3; **15**, 2595-51-9; **16**, 17604-16-9; **17**, 17604-17-0; **18**, 17604-18-1; **19**, 17604-54-5; **20**, 17604-55-6; **21**, 17604-56-7; **22**, 17604-57-8; **23**, 17659-02-8; **24**, 17604-58-9; **25**, 17604-59-0; **26**, 17604-60-3; **27**, 17604-61-4; **28**, 17604-62-5; **29**, 17604-63-6; **31**, 17604-64-7; **32**, 17604-65-8; **33**, 17604-66-9; phenyl (dimethoxyphosphinyl)acetate, 17604-67-0; 1,3-dichloro-2-(phenylthio)ethyl diethyl phosphate, 17604-68-1.

(25) C. E. Dalgliesh and F. C. Mann, *J. Chem. Soc.*, 559 (1947); *Chem. Abstr.*, **41**, 5445 (1947).