the University of Illinois, for discussions about the chemistry.

Registry No.—**1**, 1005-10-3; **2**, 934-31-6; **3**, 55052-32-9; **4a**, 55758-94-6; **4b**, 55758-95-7; **4c**, 55758-96-8; **4d**, 55758-97-9; **4d** CH_2Cl_2, 55758-98-0; **4d** tetrabromide, 55758-99-1; **4e**, 55759-00-7; **5**, 55759-01-8; **8**, 55759-02-9; **9**, 55759-03-0; **10**, 55759-04-1; **12**, 55822-52-1; $Ph_2PSCH_2CH_2P(Ph)_2C_6S_4(CN)_4$, 55759-05-2; fluoroboric acid, 16872-11-0; tributylphosphine, 998-40-3; tributylphosphine sulfide, 3084-50-2; terephthaldehyde, 623-27-0; 2-benzylidene-4,5-dicyano-1,3-dithiole, 55759-06-3; $\Delta^{2,2'}$-bi(4,5-dicyano-1,3-dithiolidene)bis(maleonitriledithiolato)nickel, 55663-96-2.

References and Notes

(1) A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, **7**, 232 (1974), and references cited therein; J. P. Ferraris, D. O. Cowan, V. Walatka, and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973); P. R. Moses and J. Q. Chambers, *Ibid.*, **96**, 945 (1974); F. Wudl, G. M. Smith, and E. J. Hufnagel *Chem. Commun.*, 1453 (1970).

(2) E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Am. Chem. Soc.*, **87**, 934 (1965); H. Hartzler, *Ibid.*, **92**, 1412 (1970); R. Okazaki, K. Okawa, and N. Imamoto, *Chem. Commun.*, 843 (1971); W. Adam and Ju-chao Liu, *J. Chem. Soc., Chem. Commun.*, 73 (1972); S. Hunig, G. Kiesslich, H. Quast, and D. Schentzow, *Justus Liebigs Ann. Chem.*, 310 (1973).

(3) E. M. Engler and V. V. Patel, *J. Am. Chem. Soc.*, **96**, 7376 (1974); K. Bechgaard, D. O. Cowan, and A. N. Bloch, *J. Chem. Soc., Chem. Commun.*, 937 (1974).

(4) E. J. Corey and G. Märkl, *Tetrahedron Lett.*, 3201 (1967).

(5) M. G. Miles, J. D. Wilson, D. J. Dahm, and J. H. Wagenknecht, *J. Chem. Soc., Chem. Commun.*, 751 (1974).

(6) D. C. Dittmer, H. E. Simmons, and R. D. Vest, *J. Org. Chem.*, **29**, 497 (1964).

(7) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. VanWazer, "P^{31} Nuclear Magnetic Resonance", Interscience, New York, N.Y., 1967, pp 238–260, 296.

(8) J. F. Blount, D. L. Coffen, and F. Wong, *J. Org. Chem.*, **39**, 2374 (1974).

(9) A referee correctly noted that a P–C–H coupling constant of 5.7 Hz is much smaller than expected for an ester of a methanephosphonic acid. In fact, the ^{31}P chemical shift (−14.6 ppm from H_3PO_4) is also smaller than would be expected for such a structure unless one takes into account the fact that substitution of second-row elements for hydrogen on the carbon α to phosphorus in these structures reduces both the chemical shift and coupling constant. The values observed for **9** compare well with those quoted[7] for, e.g., $ClCH_2PO(OCH_3)_2$ (−18.5 ppm, 8.0 Hz) and $Cl_2CHPO(OEt)_2$ (−9.3 ppm).

(10) Very recently Scherowsky and Weiland published[11] results which call into question the intermediacy of ylides such as **7** in reactions of this sort. Under their conditions, however (they studied the reactions of benzo[*d*]-1,3-dithiole-2-thione with triethyl phosphite, alone and in the presence of sundry reagents), their intermediate **14** (which corresponds to our **6**) would be expected to be more reactive than **6**, especially toward electrophilic reagents. Conversion to an ylide, in their case, is being forestalled by other reactions.

(11) G. Scherowsky and J. Weiland, *Chem. Ber.*, **107**, 3155 (1974).

(12) Cf. the easy loss of nitrogen from pyrazolidenes, 1,3,4-oxadiazolidenes, and similar species.

(13) D. L. Coffen, J. G. Chambers, D. R. Williams, P. E. Garrett, and N. O. Canfield, *J. Am. Chem. Soc.*, **93**, 2258 (1971).

(14) H. D. Hartzler, *J. Am. Chem. Soc.*, **95**, 4379 (1973).

(15) D. A. Tyssee and M. M. Baizer, *J. Electrochem. Soc.*, **118**, 1420 (1971). We thank Dr. J. H. Wagenknecht, Monsanto, for performing these experiments.

(16) We thank the Laboratory of Chemistry, National Heart and Lung Institute, for these measurements.

(17) E. Klingsberg, *J. Am. Chem. Soc.*, **86**, 5290 (1964).

(18) E. Ciganek and C. G. Krespan, *J. Org. Chem.*, **33**, 541 (1968).

(19) We thank R. Jansen of Monsanto for this measurement, performed on a CW spectrometer operating at 40.5 MHz, and referenced to external H_3PO_4.

Organophosphorus Compounds. XIII.[1a] Protonation, Cleavage, and Alkylation of Thiophosphates and Thiophosphites

George A. Olah* and Charles W. McFarland[1b,c]

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Received February 5, 1975

Protonation, cleavage, and alkylation reactions of phosphorothioic acids, $H_3PS_nO_{4-n}$ (n = 0–3), alkyl mono- and dithiophosphates, and systematically substituted phosphorothioites $P(SC_2H_5)_n(OCH_3)_{3-n}$, phosphorothiolates, $OP(SC_2H_5)_n(OCH_3)_{3-n}$, and phosphorothionates, $SP(SC_2H_5)_n(OCH_3)_{3-n}$ (n = 0–3), were studied in fluorosulfuric acid solution by ^1H and ^{31}P NMR spectroscopy (primarily at −60 to −80°). Trivalent phosphorus compounds are protonated at phosphorus, phosphoryl compounds at the phosphoryl oxygen, and thiophosphoryl compounds at the thiono sulfur atom. In the last case, the two-bond coupling, $^2J_{PSH}$, is observed below −50°. In general, sulfur is less able than oxygen to donate nonbonded electron pairs to phosphorus in the stabilization of phosphonium ions. The change in the ^{31}P chemical shift of thiophosphates and thiophosphites upon protonation is a function of the site of protonation and the relative numbers of oxygen and sulfur atoms bonded to phosphorus. Isopropoxymercaptophosphonium ions undergo rearrangements by isopropyl group migration from oxygen to sulfur. All intermediates in these processes can be individually observed.

Since our report of nuclear magnetic resonance spectroscopic studies of protonated phosphates and phosphites (oxyphosphonium ions),[1a] we have extended our work to many thiophosphorus analogs. Considering that the most important influence on the structures of the oxyphosphonium ions, as particularly revealed by their ^{31}P chemical shifts, is electron donation by the oxygen atoms to phosphorus by means of $p\pi$–$d\pi$ bond formation,[1a] our interest was in determining the relative ability of sulfur atoms bonded to phosphorus to similarly stabilize phosphonium ions. In general, phosphorus–sulfur π-bond formation is less favored geometrically than is phosphorus–oxygen π-bond formation.[2] Our expectation was that NMR spectroscopy would be a sensitive tool for determining the effects of sulfur substitution for oxygen in positively charged phosphorus intermediates.

We were particularly interested in whether the phosphorus lone electron pair (in the phosphites) is the site of protonation in strong acid solution, and otherwise whether the phosphoryl sulfur or oxygen atoms are protonated. These expectations, which were based on our work with phosphates and phosphites,[1a] would not necessarily arise from other earlier chemical observations. Trialkyl phosphorotrithioites undergo neither the Michaelis–Arbuzov reaction with alkyl or acyl halides nor the anti-Arbuzov reaction with polyhalocyclopentadienes[28] (nucleophilic attack by phosphorus). Rather, the sulfur atoms are the reactive sites, yielding, for example, dialkyl phosphorodithious halides and dialkyl sulfides in the first case,[3] and halocyclopentadienyl alkyl sulfides and the phosphorodithious halides in the second case.[29] Mixed phosphorothioites of the types $(RO)_2PSR$ and $ROP(SR)_2$ react in mixed fashion, giving products arising from both phosphorus and sulfur atom alkylation.[4] The nucleophilic reactivity of thiophosphoryl sulfur atoms has been interpreted in terms of the "hard–soft" acid–base concept,[5] with the "soft" sulfur

Table I
^{31}P and ^{1}H NMR Parameters of Protonated Alkyl Mono- and Dithiophosphates (−60 to −80°)

Phosphonium ion[e]	$\delta\ ^{31}P$ (85% H_3PO_4 = 0)			$\delta\ ^{1}H$ (J, Hz)			
				Mercapto proton(s)		α-Alkyl proton(s) ($^{3}J_{PH}$)	
	Ion	Precursor[f]	$\Delta\delta_P$[a]	Ion ($^{2}J_{PSH}$)	Precursor	Ion	Precursor
$(HS)_2P(OCH_3)_2^+$	−94.2	−89.8	−4.4	*b*	*b*	4.37 (15.6)	4.33 (15.5)
$HS(H_3CS)P(OCH_3)_2^+$	−99.6	−99.0	−0.6	4.01 (13.3)		4.34 (15.0)[c]	4.28 (15.0)[c]
						2.79 (20.3)[d]	2.81 (15.8)[d]
$(HS)_2P(OC_2H_5)_2^+$	−87.0	−84.6	−2.4	4.33 (13.9)	4.18	4.77 (9.8)	4.66 (10.5)
$HS(HO)P(OC_2H_5)_2^+$	−43.8	−58.3	+14.5	3.84 (17.2)	8.48	4.74 (8.5)	4.59 (9.7)
$(HS)_2P(O\text{-}i\text{-}C_3H_7)_2^+$	−80.1	−81.1	+1.0	4.38 (13.7)	4.07	5.41 (7.7?)	5.26 (12.5)
$(HS)_2P(O\text{-}i\text{-}C_4H_9)_2^+$	−88.1	−85.0	−3.1	4.34 (14.0)	3.98	4.46 (7.4)	4.32 (8.8)

[a] Change in δ_P upon protonation. [b] Could not be determined. [c] Methoxy protons. [d] Thiomethyl protons. [e] Registry no. are, respectively, 55649-05-3, 55649-06-4, 55649-07-5, 55649-08-6, 55649-09-7, 55649-10-0. [f] Registry no. are, respectively, 756-80-9, 2953-29-9, 298-06-6, 2465-65-8, 107-56-2, 2253-52-3.

atom showing relative disinclination to react with a "hard" proton. Schmidpeter and Brecht utilized the susceptibility of thiophosphoryl sulfur toward alkylation to methylate a series of tetravalent thiophosphorus compounds $L_n(C_6H_5)_{3-n}$ PS (L = dimethylamino, methoxy; n = 0–3), obtaining the ions $L_n(C_6H_5)_{3-n}PSCH_3^+$.[6] In this case it was suggested that the L substituents do increase their shielding of the ^{31}P nucleus (through $p\pi$–$d\pi$ contributions) upon methylation, at the expense of decreased shielding by the sulfur atom. In this paper the effects of protonation of a variety of thiophosphates and thiophosphites are examined.

Results and Discussion

Protonated Alkyl Mono- and Dithiophosphates. A series of *O,O*-dialkyl hydrogen phosphorodithioates in which the alkyl substituents were varied, as well as a closely related trialkyl phosphorodithioate (with a mercapto group replaced by a thiomethyl) and an *O,O*-dialkyl hydrogen phosphorothioate (with a mercapto group replaced by a hydroxyl group), were studied. These starting compounds were examined by ^{1}H and ^{31}P NMR spectroscopy as neat liquids at room temperature; in all cases first-order spectra were observed. The NMR parameters are summarized in Table I. The only anomaly in these spectra was that the mercapto proton in *O,O*-dimethyl hydrogen phosphorodithioate (which contained an approximately equal amount of trimethyl phosphorothiolothionate as a side product; see Experimental Section) was very difficult to observe. Possibly the peak due to this proton was obscured by peaks due to methoxy protons; the chemical shifts of the methoxy protons are in the region (δ 4.3) of mercapto proton shifts observed in other *O,O*-dialkyl hydrogen phosphorodithioates (δ 4.0–4.2). However, the ^{31}P chemical shift had the expected value. The ^{31}P chemical shift of *O,O*-diethyl hydrogen phosphorothioate (−58.3 ppm relative to 85% H_3PO_4) lies in between that of *O,O*-diethyl-*S*-methyl phosphorothioate (−28.6 ppm[7]) and that of diethylmethyl phosphorothionate (−69.6 ppm[7]). This observation can be interpreted on the basis of the hydrogen phosphorothioate somewhat preferring the thiono form, $(C_2H_5O)_2P(S)OH$, rather than the thiolo form, $(C_2H_5O)_2P(O)SH$ (the acidic protons are, of course, rapidly exchanging).

When dissolved in excess fluorosulfuric acid at low temperature (below −60°), stable ions resulting from protonation of the preceding compounds are obtained. In the ^{1}H NMR spectra, in addition to the expected alkyl proton peaks and a low-field (δ 11–12) singlet due to excess acid solvent, a doublet absorption (coupling constant 13–17 Hz) is found at δ 3.8–4.4. This doublet is attributed to thiophosphoryl sulfur atom protonation. Proton–phosphorus spin–spin coupling through one intervening sulfur atom is not commonly observed, although it has been cited in support of the formulation of bis(trifluoromethyl)phosphinothious acid as a trivalent mercapto compound ($^{2}J_{PSH}$ = 22.6 Hz).[8] Either component of the doublet observed with the protonated thiophosphates is useful for obtaining the ^{31}P chemical shift by the INDOR technique. In those cases where sufficient resolution could be achieved, the ^{31}P INDOR spectra exhibited the multiplicities expected of the protonated ions. None of the hydrogen phosphorodithioate precursors exhibit P–S–H coupling down to their freezing points.

The doublet absorptions due to the sulfur-bound protons are affected by temperature changes. Not unexpectedly, intra- and intermolecular exchange processes become more rapid at higher temperature, and the doublets coalesce in the temperature range −10 to −50°. Exchange with excess fluorosulfuric acid causes the low-field acid peak to become significantly broadened at room temperature. The doublets become increasingly sharp as the temperature is lowered; the listed ^{31}P chemical shifts of the ions, obtained by the INDOR method from the mercapto protons, and the NMR parameters of the mercapto protons were obtained at −80°. NMR parameters of the alkyl protons of the ions were obtained at −60°, where better resolution of the multiplets was found. In general, the α-alkyl protons show the expected slight deshielding upon protonation. In many cases, the ^{31}P chemical shifts of the ions were confirmed by use of the INDOR method with the α-alkyl proton peaks. As a rule, the ^{31}P shifts move to higher field by several tenths of a part per million in going from −80 to −60°.

The phosphorus nuclei in these phosphorodithioates undergo only small shifts upon protonation. This finding is characteristic of the protonation of phosphorothiolothionates, as will be seen in a later section. As also will be seen, the upfield shift of 14.5 ppm upon protonation of *O,O*-diethyl hydrogen phosphorothioate is more like the change undergone by phosphorothionates as compared to phosphorothiolates. Protonated *O,O*-diisopropyl hydrogen phosphorodithioate (diisopropoxydimercaptophosphonium ion) is the first intermediate in a series of cleavage and alkylation reactions in fluorosulfuric acid solution. These are discussed in the next section.

Protolytic Cleavage of *O,O*-Diisopropyl Hydrogen Phosphorodithioate and Triisopropyl Phosphorothionate in Fluorosulfuric Acid. It was earlier observed by us[1a] that protonated isopropyl phosphates and phosphites are quite sensitive to dealkylation, even at low temperature. One would expect that *O*-isopropyl phosphorothioates

Table II
^{31}P and ^{1}H NMR Parameters of Protonated Isopropyl Phosphorothioates, $(HS)_w(i\text{-}C_3H_7S)_xP(OH)_y(O\text{-}i\text{-}C_3H_7)_z^+$

Registry no.	w	x	y	z	$\delta_{^{31}P}$ (85% H_3PO_4 = 0)	Mercapto proton(s) $\delta_{^1H}$	Mercapto proton(s) $^2J_{PSH}$, Hz	Temp, °C
	2	0	0	2	−80.1	4.38	13.7	−80
55649-11-1	2	0	1	1	−82.4	4.46	14.3	−80
55649-12-2	2	0	2	0	−83.8	4.59	14.6	−80
55649-13-3	1	1	2	0	−86.1	4.32	13.9	−80
55649-14-4	0	2	2	0	−87.8			0
55649-15-5	1	0	0	3	−36.7	3.83	16.3	−60
55649-16-6	1	0	1	2	−39.2	3.87	16.7	−60
55649-17-7	1	0	2	1	−41.2	3.96	17.0	−60
55649-18-8	1	0	3	0	−43.0	4.05	17.2	−60
55649-19-9	0	1	3	0	−44.8			−20

would behave similarly. This is found to be the case with *O,O*-diisopropyl hydrogen phosphorodithioate. All intermediates resulting from sequential protolytic carbon–oxygen bond cleavage can be observed in the proton spectra, since the mercapto protons in each intermediate can be individually distinguished.

$$(HS)_2P(O\text{-}i\text{-}C_3H_7)_2^+ \rightarrow (HS)_2P(OH)O\text{-}i\text{-}C_3H_7^+ \rightarrow (HS)_2P(OH)_2^+$$

$$HSP(O\text{-}i\text{-}C_3H_7)_3^+ \rightarrow HS(HO)P(O\text{-}i\text{-}C_3H_7)_2^+ \rightarrow HS(HO)_2PO\text{-}i\text{-}C_3H_7^+ \rightarrow HSP(OH)_3^+$$

These processes take place fairly slowly at −60°, and ^{31}P chemical shifts of each ion were obtained by the INDOR technique utilizing the mercapto proton peaks. The cleaved isopropyl groups form isopropyl fluorosulfate and can be identified as such (in part, by ^{19}F NMR spectroscopy).

The protonated phosphorothioic acids which are formed, $(HS)_2P(OH)_2^+$ and $HSP(OH)_3^+$, take part in further reactions. Upon standing, the methine proton resonance of isopropyl fluorosulfate (δ 5.5–5.6) is seen to move substantially upfield (to δ 4.0–4.1). In keeping with Teichmann and Hilgetag's generalization of thiophosphoryl sulfur atoms showing greater nucleophilic reactivity toward carbon centers rather than protons,[5] isopropyl fluorosulfate alkylates the sulfur atoms of protonated phosphorothioic acids.

$$(HO)_2P(SH)_2^+ \rightarrow (HO)_2P(SH)S\text{-}i\text{-}C_3H_7^+ \rightarrow (HO)_2P(S\text{-}i\text{-}C_3H_7)_2^+$$

$$(HO)_3PSH^+ \rightarrow (HO)_3PS\text{-}i\text{-}C_3H_7^+$$

Under these reaction conditions the mercaptophosphonium ions are more nucleophilic toward the isopropyl group than are fluorosulfate ions. The methine protons exhibit three-bond coupling to phosphorus ($^3J_{PSCH}$), allowing ^{31}P INDOR observations to be made in those cases where no mercapto proton can be so utilized. The end result of the multistep reactions that the protonated *O*-isopropyl phosphorothioates undergo is rearrangement of the alkyl substituents from oxygen to sulfur. These reactions are closely related to the well-known thiono–thiolo rearrangement equilibria of neutral phosphorothionate esters,[9] and in mechanism are similar to the alkyl exchange reactions of phosphorothionates with alkyl halides.[10] The alkyl exchange reactions usually require vigorous conditions,[5] but in our work the strong acid facilitated rearrangements can be followed by NMR spectroscopy at 0°. The ease of rearrangement of the *O*-isopropyl phosphorothioates in fluorosulfuric acid solution arises from the facile carbon–oxygen bond cleavage at even lower temperature.[11]

The NMR parameters of all of the isopropyl phosphorothioate intermediates are summarized in Table II. In each protonated phosphorothioate the phosphorus nucleus becomes increasingly deshielded as each *O*-isopropyl group is cleaved off and (later) becomes attached to a sulfur atom. It is of interest to note that the phosphorus in triisopropyl phosphorothionate (δ_P −64.5) becomes substantially more shielded upon protonation ($\Delta\delta_P$ +27.8). This is characteristic of trialkyl phosphorothionates, as discussed subsequently.

Protonation of Systematically Substituted Phosphorothioites, Phosphorothiolates, and Phosphorothionates. A suitable way of determining the relative charge-delocalizing abilities of sulfur and oxygen in phosphonium ions is to study systematically substituted series of compounds. One can look for general trends in, for example, NMR parameters as oxygen substituents are successively replaced by sulfur substituents. Accordingly, a series of phosphorothioites, $(C_2H_5S)_nP(OCH_3)_{3-n}$, phosphorothiolates, $(C_2H_5S)_nP(O)(OCH_3)_{3-n}$, and phosphorothionates, $(C_2H_5S)_nP(S)(OCH_3)_{3-n}$, were prepared; NMR spectra of these compounds and of the phosphonium ions which result from protonation in fluorosulfuric acid solution have been obtained. The parameters involving phosphorus and the protons closest to it are summarized in Table III. The precursor compounds were all examined as neat liquids at room temperature. The NMR spectra were all interpreted on a first-order basis. The methoxy proton resonance signals, or (if no methoxy protons were present) the ethylthio methylene proton signals, were utilized to obtain ^{31}P chemical shifts by the INDOR technique.

We have so far been unable to prepare one desired precursor, *S*-ethyl-*O,O*-dimethyl phosphorothioite. Although the synthesis of the triethyl analog has been reported,[4] NMR spectroscopic data for trialkyl phosphorothioites are quite scanty.[13] Several attempts to prepare the ethyldimethyl phosphorothioite by usual methods were made, but only mixtures of products were obtained (see Experimental Section). In order to obtain a dialkoxythiophosphonium ion, diethyl phosphonothionate was prepared (^{31}P shift found to be −68.8 ppm) and protonated (δ_P −64.3).

In certain of the ethyl thiophosphates and thiophosphites, the methylene protons are magnetically nonequivalent owing to molecular asymmetry. This asymmetry is present in molecules of the type, among others, $CH_3CH_2(O$ or S) PXYZ, where X, Y, and Z are different from each other.[14] X, Y, and Z can be, as in this work, oxygen, sulfur, alkoxy groups, alkylthio groups, or a lone electron pair. However, the nonequivalence of the methylene protons is not always observed. In this work, diethyl phosphonothionate and *S,S*-diethyl-*O*-methyl phosphorodithioite demonstrated magnetic nonequivalence by a slight irregular splitting of the methylene proton resonance peaks. Each com-

Table III
^{31}P and ^{1}H NMR Parameters of Protonated Phosphorothioites, $HP(SC_2H_5)_n(OCH_3)_{3-n}^+$, Phosphorothiolates, $HOP(SC_2H_5)_n(OCH_3)_{3-n}^+$, and Phosphorothionates, $HSP(SC_2H_5)_n(OCH_3)_{3-n}^+$ (−60 to −80°)

		$\delta_{^{31}P}$ (85% H_3PO_4 = 0)			$\delta_{^{1}H}$ (J, Hz)					
					PH proton	Mercapto	O-Methyl protons ($^3J_{POCH}$)		S-Methylene protons ($^3J_{PSCH}$)	
Precursor class	n	Ion[g]	Precursor[h]	$\Delta\delta_P$[a]	($^1J_{PH}$)	proton ($^2J_{PSH}$)	Ion	Precursor	Ion	Precursor
Phosphorothioites	0[b]	−24.7	−139.7	+115.0	7.47 (827)		4.34 (12.1)	3.66 (10.8)		
	1	(−75)[c]	(−152)[d]	(+77)	[8.36 (761)][e]		*f*	*f*	*f*	*f*
	2	−87.8	−160.8	+73.0	8.85 (678)		4.23 (16.3)	3.88 (8.8)	3.46 (17.8)	3.16 (10.5)
	3	−63.3	−114.7	+51.4	8.69 (594)				3.41 (19.5)	3.29 (9.3)
Phosphorothiolates	0[b]	−2.0	−2.3	+0.3			4.42 (11.5)	4.15 (11.2)		
	1	−51.2	−30.0	−21.2			4.32 (12–13)	4.18 (12.7)	~3.33 (*f*)	3.27 (15.2)
	2	−96.7	−58.7	−38.0			4.33 (14.7)	4.28 (14.0)	3.36 (19.2)	3.40 (16.4)
	3	−118.6	−59.9	−58.7					3.42 (18.7)	3.48 (15.9)
Phosphorothionates	0	−50.2	−72.8	+22.6		3.82 (17.0)	4.34 (13.4)	4.13 (13.7)		
	1	−97.7	−99.3	+1.6		4.08 (13.0)	4.33 (15.0)	4.18 (15.2)	3.41 (19.9)	3.30 (16.6)
	2	−121.3	−112.4	−8.9		4.44 (11–14)	4.29 (17.4)	4.27 (16.0)	3.46 (19.2)	3.48 (17.4)
	3	−107.9	−91.5	−16.4		4.28 (12.7)			3.41 (19.2)	3.49 (17.5)

[a] Change in δ_P upon protonation. [b] Data from ref 1a. [c] Estimated from $(C_2H_5O)_2PH(SH)^+$ (δ_P −64.3). See text. [d] Estimated by comparison with the corresponding phosphorothiolate and thiolothionate. [e] Data on $(C_2H_5O)_2PH(SH)^+$. [f] Not available or could not be determined. [g] Registry no. are, respectively, 24151-48-2, 55649-20-2, 55649-21-3, 55649-22-4, 28180-50-9, 55649-23-5, 55649-24-6, 55649-25-7, 55649-26-8, 55649-27-9, 55649-28-0, 55649-29-1. [h] Registry no. are, respectively, 121-45-9, 20472-57-5, 20472-56-4, 688-62-0, 512-56-1, 6389-81-7, 22082-34-4, 1486-39-1, 152-18-1, 3347-21-5, 22082-28-6, 1642-43-9.

ponent split in this way in actuality consists of the central doublet of an AB quartet (if the ethyl group is considered to be an ABX_3 system, with the phosphorus nucleus causing further first-order splitting).[15] From this point of view, assuming J_{AB} is 10 Hz (as is found in ethyl sulfoxy compounds possessing similar asymmetry),[14b,d] the chemical shift between the A and B protons is no more than 0.053 ppm, and the intensity of the unobserved outer lines of each AB quartet is no more than 6% of the corresponding observed central doublet.[16] The ^1H spectrum of the ethyl group is most accurately analyzed as an ABC_3 system[14b] but no significant error results in obtaining parameters by treating the methylene protons as equivalent.

Precursors were dissolved in excess fluorosulfuric acid to form a homogeneous solution. The ^1H spectra at low temperature (−60 to −80°) indicated, in addition to the presence of solvent fluorosulfuric acid, the stable ions resulting from protonation of the precursors. The tabulated parameters (Table III) of the ions were generally obtained at −60°; the methoxy proton (or, if necessary, the *S*-methylene proton) resonance peaks were used to obtain (by the INDOR method) ^{31}P chemical shifts. The ^{31}P shifts were checked by obtaining them also from INDOR experiments involving peaks due to phosphorus-bound protons or mercapto protons. Parameters involving the mercapto protons (in protonated phosphorothionates) were obtained at −80°, at which temperature splitting due to $^2J_{PSH}$ is better resolved.

All of the phosphorothioites are protonated at phosphorus. The proton bound to phosphorus produces a characteristic widely separated doublet in the ^1H spectrum due to the large one-bond coupling constant, $^1J_{PH}$. $^1J_{PH}$ decreases as ethylthio substituents replace methoxy substituents. Neither the ions nor the precursors show a regular trend in the ^{31}P chemical shifts, but the changes upon protonation are quite significant. The phosphorus nuclei become substantially shielded upon protonation, and such shielding increases with each additional methoxy substituent. The large shielding effect of protonation in trimethyl phosphite was attributed by us earlier[1a] to extensive electron donation by the oxygen atoms to phosphorus. It seems clear that sulfur is less able to effect this, so that the change in the ^{31}P shift upon protonation ($\Delta\delta_P$) is less positive as ethylthio substituents replace methoxy substituents. Nevertheless, even with triethyl phosphorotrithioite, $\Delta\delta_P$ remains large and positive.

Since *S*-ethyl-*O,O*-dimethyl phosphorothioite could not be prepared, an estimate of its ^{31}P shift was based on the known phosphorothiolate and thiolothionate. In order to estimate the ^{31}P shift of the protonated species, the closely related protonated diethyl phosphonothionate was prepared. Estimates of the effect on the ^{31}P shift of replacing the ethoxy groups by methoxy groups, and of replacing the mercapto group by a thioethyl group, were made from observations on $(CH_3O)_2P(SH)_2^+$, $(C_2H_5O)_2P(SH)_2^+$, and $(CH_3O)_2P(SH)SC_2H_5^+$. The magnetic nonequivalence of

the methylene protons observed in diethyl phosphonothionate and *S,S*-diethyl-*O*-methyl phosphorodithioite could not be seen in the corresponding protonated species. Nor was in protonated diethyl phosphonothionate the theoretically possible three-bond H–P–S–H coupling observed.

Protonation of the phosphorothiolates is not directly observable, as is usual with phosphoryl compounds.[1a] However, as arguments have been presented for the protonation of trimethyl phosphate in fluorosulfuric acid solution,[1a] it is expected that ethylthio phosphoryl compounds are also capable of being protonated. Except for trimethyl phosphate, which shows a small positive value, $\Delta\delta_P$ becomes increasingly negative as ethylthio groups replace methoxy groups. This trend indicates that the electron donation to phosphorus by the fully formed phosphoryl bond in the precursors cannot be maintained upon protonation. Again, sulfur is less capable than oxygen of providing such donation in the phosphonium ions.

Protonation of the phosphorothionates can be observed directly at low temperature. The thiophosphoryl sulfur atom is the site of protonation; the two-bond coupling of the donated proton, $^2J_{PSH}$, is distinct. The ^{31}P shifts of the ions compare well with known shifts of related ions: $(CH_3O)_3PSH^+$ (δ_P −50.2) is close to $(CH_3O)_3PSCH_3^+$ (−53.2), and $(C_2H_5S)_3PSH^+$ (−107.9) is in the same region as a value assigned to $P(SC_6H_5)_4^+$ (−121.8).[17] As before, $\Delta\delta_P$ is the quantity which exhibits a regular trend. $\Delta\delta_P$ is substantially positive in the case of trimethyl phosphorothionate, decreasing in value and becoming negative as ethylthio groups replace methoxy groups. With one or two sulfur atoms attached to phosphorus, protonation permits increased electron donation by the remaining oxygen atoms through $p\pi$–$d\pi$ bond formation. With three or four sulfur substituents, there are not enough oxygen substituents to counteract the loss of shielding by the thiophosphoryl sulfur atom (fairly weak compared to an oxygen atom) upon protonation.

An interesting correlation between the protonated phosphorothiolates and the protonated phosphorothionates is that, regardless of whether phosphoryl oxygen or thiophosphoryl sulfur atom protonation is involved, the ^{31}P shifts of the ions are determined largely (within 3 ppm) by the relative numbers of oxygen and sulfur atoms attached to phosphorus. Compare, for example, $(C_2H_5S)_2(CH_3O)POH^+$ (δ_P −96.7) and $(C_2H_5S)(CH_3O)_2PSH^+$ (−97.7). The shifts of the precursors are quite different, of course, since there is a considerable difference in the amount of π bonding in a phosphoryl group as contrasted with a thiophosphoryl group. Protonation of either decreases π bonding. Other phosphorus-bound oxygen and sulfur atoms increase this contribution. Changes in ^{31}P shifts appear to be strongly affected by oxygen's greater tendency toward back-bonding.

Protonated Phosphorothioic Acids. As was pointed out earlier, among the cleavage products observed in solutions of isopropyl phosphorothioates in fluorosulfuric acid are protonated phosphorothioic acid (trihydroxymercaptophosphonium ion) and protonated phosphorodithioic acid (dihydroxydimercaptophosphonium ion). Since data on protonated phosphoric acid were available from our earlier work,[1a] it was desirable to obtain protonated phosphorotrithioic acid and protonated phosphorotetrathioic acid to complete the series of protonated phosphorothioic acids (hydroxymercaptophosphonium ions). These ions are the parent acids of all of the protonated thiophosphates. It was expected that if these ions could be produced in acid solution, the two-bond P–S–H coupling could be utilized to obtain ^{31}P chemical shifts by the INDOR method.

Table IV
^{31}P and ^1H NMR Spectral Parameters of Protonated Phosphorothioic Acids, $(HS)_nP(OH)_{4-n}^+$ (−80°)

		$\delta_{^{31}P}$ (85% H_3PO_4 = 0)		$\delta_{^1H}$, mercapto proton(s) ($^2J_{PSH}$, Hz)
n	Ion	Precursor,[a] $(PS_nO_{4-n})^{3-}$	$\Delta\delta_P$[b]	
0	−2.3[c]	0	−2	
1	−43.0	−32	−11	4.05 (17.2)
2	−83.8	−61	−23	4.59 (14.6)
3	−118.2	−86	−32	4.25 (11.4)

[a] L. Maier and J. R. Van Wazer, *J. Am. Chem. Soc.*, 84, 3054 (1962). Registry no., 29602-99-8; 55660-12-3. [b] Change in δ_P upon protonation. [c] From ref 1a.

The sodium salts of phosphorotrithioic and phosphorotetrathioic acids contain too much water of crystallization ($Na_3POS_3 \cdot 11H_2O$ and $Na_3PS_4 \cdot 8H_2O$)[18] for substantial hydrolysis to be prevented in acid solution. Protonated phosphorotrithioic acid was obtained by preparing tri-*tert*-butyl phosphorotrithiolate and dissolving it in fluorosulfuric acid. Expectedly, considering the nucleophilicity of the sulfur atoms, the trithiolate demonstrated considerable resistance to carbon–sulfur bond cleavage in acid solution. However, allowing the acid solution to stand at room temperature for 20 min resulted in the *tert*-butyl substituents being cleaved to form *tert*-butyl cations (which tend to deprotonate and escape as methylpropene vapor), leaving the desired hydroxytrimercaptophosphonium ion. Its NMR spectral data are included in a summary of protonated phosphorothioic acids (Table IV). Again, the change in the ^{31}P chemical shift upon protonation correlates very well with the number of oxygen and sulfur atoms bonded to phosphorus.

We have so far been unable to prepare tri-*tert*-butyl phosphorotetrathioate[19] in sufficiently pure form so as to obtain the tetramercaptophosphonium ion by similar alkyl group cleavage.

For the protonated thiophosphates and thiophosphites in this paper, the size of the coupling constant $^2J_{PSH}$ (11–17 Hz) permits one to estimate that, below the coalescence temperatures (−10 to −50°), proton exchange in FSO_3H solution takes place less than 25–38 times per second.[20]

Experimental Section

NMR Spectra. ^1H and ^{31}P nuclear magnetic resonance spectroscopic techniques have been earlier described by us.[1a]

Preparation of the Ions. Phosphorus compounds were dissolved in a tenfold molar excess of fluorosulfuric acid whenever possible. Stirring and cooling with a Dry Ice–acetone bath was almost always used to prevent decomposition of the protonated species. The phosphonium ions were kept at low temperature (below −60°), since most of them were observed to react further at room temperature.

Materials. We thank Dr. Alexis A. Oswald (Exxon Research and Engineering Co., Linden, N.J.) for samples of *O,O*-dialkyl hydrogen phosphorodithioates and *O,O*-diethyl hydrogen phosphorothioate. They were vacuum distilled before use. It was found by ^1H and ^{31}P INDOR spectroscopy that the *O,O*-dimethyl hydrogen phosphorodithioate contained an approximately equal amount of trimethyl phosphorothiolothionate which could not be separated by distillation. Triisopropyl phosphorothionate, trimethyl phosphorothionate, and *S,S*-diethyl-*O*-methyl phosphorotrithioate were prepared by refluxing the corresponding phosphite with sulfur in carbon disulfide solution.[21] The preparation of the phosphorothioites was based on the preparation of tertiary phosphites from phosphorus trichloride and the appropriate alcohol in the presence of *N,N*-dimethylaniline.[22] To obtain *S,S*-diethyl-*O*-methyl phosphorodithioite, phosphorus trichloride was first com-

bined with 2 mol of ethanethiol, then with 1 mol of methanol. Similarly, 3 mol of ethanethiol was used to obtain triethyl phosphorotrithioite.[23] However, attempts to make *S*-ethyl-*O,O*-dimethyl phosphorothioite were unsuccessful. Combining phosphorus trichloride with first 2 mol of methanol, then 1 mol of ethanethiol, or in the reverse order, yielded fractions distilling over a wide temperature range (30–81°, 0.02–8.0 mm). The lower boiling fractions consisted primarily of dimethyl phosphonate; higher boiling fractions contained *S*-ethyl-*O,O*-dimethyl phosphorothioate and *S*-ethyl-*O,O*-dimethyl phosphorodithioate. Treating freshly prepared ethyl phosphorodichloridothioite[24] with methanol led to similar results. Diethyl phosphonothionate was prepared by the reaction of distilled commercial diethyl phosphorochloridite with hydrogen sulfide in the presence of pyridine.[25] *S,S*-Diethyl-*O*-methyl phosphorodithioate resulted from air oxidation of the corresponding phosphite. Triethyl phosphorotrithiolate occurred as a high-boiling fraction in the distillation of the corresponding phosphite. Since it was found that sulfur does not add to this phosphite, triethyl phosphorotetrathioate was prepared by reaction of the sodium salt of ethanethiol with thiophosphoryl chloride.[26] Contrary to a statement in the reference, vacuum distillation of the product did not degrade it to triethyl phosphorotrithioite. Preparations of sodium phosphorotrithioate, sodium phosphorotetrathioate, and tri-*tert*-butyl phosphorotetrathioate were referred to earlier.[18,19] Extended refluxing of 2-methyl-2-propanethiol with phosphorus trichloride produced, not tri-*tert*-butyl phosphorotrithioite as has been indicated,[27] but pure tri-*tert*-butyl phosphorotrithiolate (as indicated by its ^{31}P NMR spectrum, particularly the chemical shift). Commercially available fluorosulfuric acid was twice distilled before use in the preparation of solutions.

Acknowledgment. Support of our work by the National Institutes of Health and by a Public Health Service Fellowship from the National Institute of General Medical Sciences (to C.W.M.) is gratefully acknowledged.

References and Notes

(1) (a) Part XII: G. A. Olah and C. W. McFarland, *J. Org. Chem.*, **36**, 1374 (1971). (b) National Institutes of Health Predoctoral Research Fellow, 1968–1970. (c) Taken in part from the Ph.D. Dissertation of C. W. McFarland, Case Western Reserve University, 1971.
(2) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry", Academic Press, New York, N.Y., 1965, Chapter 3.
(3) A. F. Divinskii, M. I. Kabachnik, and V. V. Sidorenko, *Dokl. Akad. Nauk SSSR*, **60**, 999 (1948).
(4) A. E. Arbuzov and K. V. Nikonorov, *Dokl. Akad. Nauk SSSR*, **62**, 75 (1948).
(5) H. Teichmann and G. Hilgetag, *Angew. Chem., Int. Ed. Engl.*, **6**, 1013 (1967).
(6) A. Schmidpeter and H. Brecht, *Z. Naturforsch., Teil B*, **24**, 179 (1969).
(7) G. H. Birum in M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, "P^{31} Nuclear Magnetic Resonance", Wiley, New York, N.Y., 1967, pp 344, 369.
(8) R. G. Cavell and H. J. Emeléus, *J. Chem. Soc.*, 5825 (1964).
(9) Reference 2, pp 122–123.
(10) (a) P. Pistschimuka, *J. Prakt. Chem.*, **84**, 746 (1911); (b) P. S. Pistschimuka, *Zh. Russ. Fiz.-Khim. Chast Khim.*, **44**, 1406 (1912); *Chem. Abstr.*, **7**, 987 (1913).
(11) The rearrangement of phosphorothionates is also greatly enhanced by the use of Lewis acids such as $SnCl_4$, $SnBr_4$, $FeCl_3$, $AlCl_3$, $TlCl_4$, and BF_3.[12]
(12) (a) H. Teichmann and G. Hilgetag, *Chem. Ber.*, **98**, 856 (1965); (b) G. Hilgetag, H. Teichmann, and M. Krüger, *Ibid.*, **98**, 864 (1965); (c) L. Elegant, J. F. Gal, and M. Azzaro, *Bull. Soc. Chim. Fr.*, 4273 (1969), and references cited therein.
(13) (a) Reference 7, Chapter 4; (b) P. G. Maslov, *J. Phys. Chem.*, **72**, 1414 (1968).
(14) (a) H. Finegold, *J. Am. Chem. Soc.*, **82**, 2641 (1960); (b) F. Kaplan and J. D. Roberts, *Ibid.*, **83**, 4666 (1961); (c) T. H. Siddall, C. A. Prohaska, and W. E. Shuler, *Nature (London)* **190**, 903 (1961); (d) J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961).
(15) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Vol. 1, Pergamon Press, Elmsford, N.Y., 1965, p 368.
(16) Reference 15, p 319.
(17) S. C. Peake and R. Schmutzler, *J. Chem. Soc. A*, 1049 (1970).
(18) G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry", Vol. 1, 2nd ed, Academic Press, New York, N.Y., 1963, pp 571–573.
(19) W. A. Schulze, G. H. Short, and W. W. Crouch, *Ind. Eng. Chem.*, **42**, 916 (1950).
(20) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds", Prentice-Hall, Englewood Cliffs, N.J., 1965, p 71.
(21) G. M. Kosolapoff, "Organophosphorus Compounds", Wiley, New York, N.Y., 1950, pp 235–236.
(22) H. McCombie, B. C. Saunders, and G. J. Stacey, *J. Chem. Soc.*, 380 (1945).
(23) A. Lippert and E. E. Reid, *J. Am. Chem. Soc.*, **60**, 2370 (1938).
(24) Reference 21, p 180.
(25) R. Sallmann, U.S. Patent 2,805,241 (1957).
(26) R. A. McIvor, G. D. McCarthy, and G. A. Grant, *Can. J. Chem.*, **34**, 1819 (1956).
(27) W. W. Crouch and R. T. Werkman, U.S. Patent 2,682,554 (1954).
(28) V. Mark, *Tetrahedron Lett.*, 295 (1961); B. Miller, *Top. Phosphorus Chem.*, **2**, 174 (1965).
(29) V. Mark, Abstracts, 142nd National Meeting of the American Chemical Society, Atlantic City, N.J., Sept 1962, No. ORGN-57; U.S. Patent 3,106,586 (1964); *Chem. Abstr.*, **60**, 5358 (1964); B. Miller, *Top. Phosphorus Chem.*, **2**, 175–176 (1965).

Nucleophilic Displacements on Halogen Atoms. V. Reactions of α-Halo Sulfones with Sterically Hindered Nucleophiles

Bruce B. Jarvis* and Bruce A. Marien

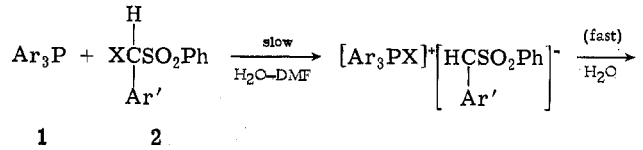
Department of Chemistry, University of Maryland, College Park, Maryland 20742

Received April 11, 1975

The rates of reaction of α-bromo- and α-iodo-*m*-cyanobenzyl phenyl sulfones (3) with a number of sterically hindered phosphines in aqueous DMF are reported. The variation in rates for tris(*o*-tolyl)phosphine (4) and tris(*o*-anisyl)phosphine (5) with **3a** is best explained in terms of a steric rather than special electronic effect. The reactions of 3 with *cis*-bis(diphenylphosphino)ethene (8) and bis(diphenylphosphino)ethane (11) exhibit no unusual characteristics.

The reductions of α-halobenzyl phenyl sulfones by triarylphosphines has been shown to involve nucleophilic attack on the halogen atom (eq 1).[1–3] Hydrolysis of the charged complex yields the phosphine oxide, the reduced sulfone, and a hydrohalic acid.

In these reports it was observed that, contrary to the normal SN2 reaction at carbon atoms, the reactivity decreased in the order α-Br > α-I ≫ α-Cl. The anomalous behavior of the α-iodobenzyl phenyl sulfones was rationalized in terms of the relative strengths of the bonds formed and broken upon entering the transition state.



1 **2**

$$HX + Ar_3P{=}O \quad Ar'CH_2SO_2Ph \qquad (1)$$

It has been demonstrated that this reaction is strongly dependent upon the electron-withdrawing ability of the parent sulfone.[2] ρ values, determined from the variation of