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THE REDUCTION OF SEMIPOLAR LINKAGES BY O,O-DIALKYL DITHIOPHOSPHORIC ACID[1]

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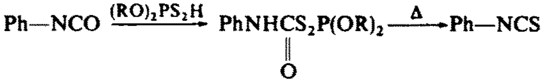
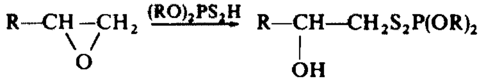
Abstract—Compounds having a semipolar functional group, generally formulated X → Y, i.e. sulfoxide, sulfilimine, sulfonium ylide, pyridine N-oxide, and N-iminopyridinium betaine, were found to react readily with O,O-dialkyl dithiophosphoric acid to afford the corresponding reduction products, sulfide and pyridine.

INTRODUCTION

For a long time O,O-dialkyl dithiophosphoric acid derivatives have been used as pesticides, insecticides, oil additives, and in many other ways. There have been also numerous reports on the reactions of dithiophosphoric acid itself. For example, dithiophosphoric acid was shown to give phenylisothiocyanate with phenyl isocyanate (Eq. 1),[2] and to react with epoxide to give the corresponding open-chain hydroxyalkyl ester of dithiophosphoric acid (Eq. 2).[3]

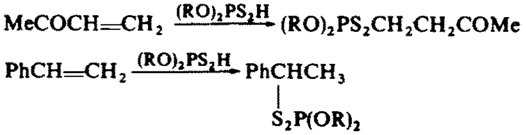


$$\mathrm{Ph{-}NCO} \xrightarrow{(\mathrm{RO})_2\mathrm{PS}_2\mathrm{H}} \mathrm{PhNH}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{S_2P(OR)_2} \xrightarrow{\Delta} \mathrm{Ph{-}NCS} \qquad (1)$$



(2)

Detailed studies of addition reactions of O,O-dialkyl dithiophosphoric acid to carbon–carbon multiple bonds have also been carried out (Eq. 3).[4]

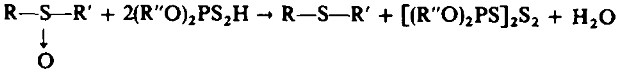


$$\begin{aligned}&\mathrm{MeCOCH{=}CH_2} \xrightarrow{(\mathrm{RO})_2\mathrm{PS}_2\mathrm{H}} \mathrm{(RO)_2PS_2CH_2CH_2COMe}\\&\mathrm{PhCH{=}CH_2} \xrightarrow{(\mathrm{RO})_2\mathrm{PS}_2\mathrm{H}} \mathrm{Ph}\underset{\underset{\mathrm{S_2P(OR)_2}}{|}}{\mathrm{CH}}\mathrm{CH_3}\end{aligned} \qquad (3)$$

Previously[5] we reported the reduction of a few representative sulfoxides and sulfilimines by the use of O,O-dialkyl dithiophosphoric acid. Here we describe a detailed investigation of this apparent reduction of sulfoxides, sulfilimines and other compounds having a semipolar linkage such as sulfonium ylides, tertiary amine N-oxides, and N-iminopyridinium betaines.

RESULTS

The reaction of sulfoxides and sulfilimines with O,O*-dialkyl dithiophosphoric acid.* Sulfoxides and N-*p*-toluenesulfonylsulfilimines were found to react with O,O-dialkyl dithiophosphoric acid to give quantitatively bis[O,O-dialkyl thiophosphoryl]-disulfide and the corresponding reduction product, i.e. sulfide and N-*p*-tolenesulfonamide, (Table I, Eq. 4–5). The reduction of sulfoxides and N-*p*-toluenesulfonylsulfilimines by trivalent phosphorus compounds[6] and other reducing agents[7] has recently been investigated, and in most cases the reaction requires rather high temperatures. However, O,O dialkyl dithiophosphoric acids are easily oxidized to the



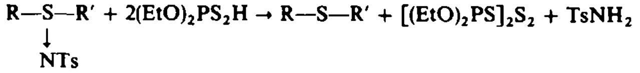
$$\underset{\displaystyle O}{\underset{\downarrow}{R{-}S{-}R'}} + 2(R''O)_2PS_2H \rightarrow R{-}S{-}R' + [(R''O)_2PS]_2S_2 + H_2O \quad (4)$$

(1a–e)
a: R = R′ = Me
b: R = Ph, R′ = Me
c: R = Ph, R′ = Et
d: R = Ph, R′ = CH$_2$Ph
e: R = R′ = Ph

(2a–b)
a: R″ = Et
b: R″ = i—Pr

(3a–e)
a: R = R′ = Me
b: R = Ph, R′ = Me
c: R = Ph, R′ = Et
d: R = Ph, R′ = CH$_2$Ph
e: R = R′ = Ph

(4a–b)
a: R″ = Et
b: R″ = i—Pr



$$\underset{\displaystyle NTs}{\underset{\downarrow}{R{-}S{-}R'}} + 2(EtO)_2PS_2H \rightarrow R{-}S{-}R' + [(EtO)_2PS]_2S_2 + TsNH_2 \quad (5)$$

(5a–c)
a: R = R′ = Me
b: R = Ph, R′ = Me
c: R = R′ = Ph

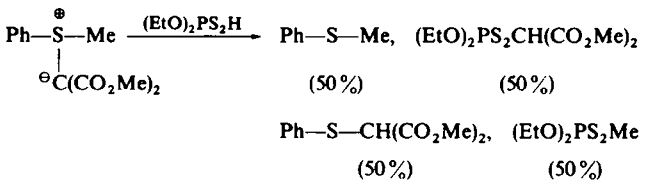
TABLE I. REDUCTION OF SULFOXIDES AND SULFILIMINES BY O,O-DIALKYL DITHIOPHOSPHORIC ACID AT ROOM TEMPERATURE[a]

Compound	Reducing Agent	Solv.	Reac. Time (hr)	Product
1a[b]	PhSH	None	12	**3a**, PhSSPh, H_2O[c]
1a	**2a**	None	0·25	**3a**, **4a**, H_2O
1a[d]	**2b**	None	0·25	**3a**, **4b**, H_2O
1b	**2a**	None	0·25	**3b**, **4a**, H_2O
1c	**2a**	$CHCl_3$	12	**3c**, **4a**, H_2O
1d	**2a**	$CHCl_3$	12	**3d**, **4a**, H_2O
1e[d]	**2a**	None	12	**3e**, **4a**, H_2O
5a	**2a**	None	0·25	**3a**, **4a**, $TsNH_2$
5b	**2a**	None	0·25	**3b**, **4a**, $TsNH_2$
5c	**2a**	None	0·25	**3e**, **4a**, $TsNH_2$

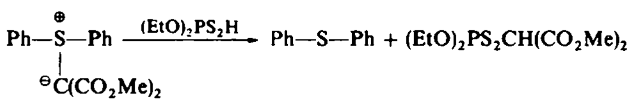
[a] Yields nearly quantitatively.
[b] Carried out at 80°.
[c] Water was not identified.
[d] Also been reported by Mikolajczyk *et al.*[8]

corresponding bis[O,O-dialkyl thiophosphoryl]disulfide by various sulfoxides and sulfilimines nearly quantitatively even at room temperature without any side reaction. Since O,O-dialkyl dithiophosphoric acids are markedly more acidic [e.g. $(EtO)_2PS_2H$, $pKa = 1{\cdot}62$; $(i\text{-}PrO)_2PS_2H$, $pKa = 1{\cdot}82$; $(PrO)_2PS_2H$, $pKa = 1{\cdot}75$; $(BuO)_2PS_2H$, $pKa = 1{\cdot}83$][9] than either thiophenol ($pKa = 7{\cdot}47$[10]) or phosphoric acid ($pKa = 2{\cdot}00$[11]), it is anticipated in view of the mechanism postulated by Wallace *et al.*[12] that O,O-dialkyl dithiophosphoric acid is more reactive than weakly acidic thiophenol. In fact, the reaction of dimethyl sulfoxide with thiophenol to give dimethyl sulfide and diphenyl disulfide requires 12 hours at 80° (Table I). A similar reaction between dimethyl sulfoxide and O,O-dialkyl dithiophosphoric acid is completed in 15 min. even at room temperature. Thus, O,O-dialkyl dithiophosphoric acids are excellent reducing agents for sulfoxides and sulfilimines.

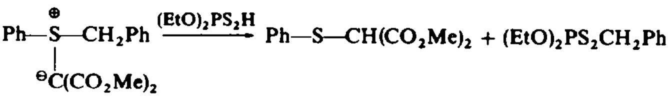
The reaction of sulfonium bis(carbomethoxy)methylide with O,O-*diethyl dithiophosphoric acid.* Since sulfonium ylides are isoelectronic to sulfoxides and sulfilimines, they are anticipated to react in similar manner with O,O-dialkyl dithiophosphoric acid. Phenyl methyl sulfonium bis(carbomethoxy)methylide was found to react with O,O-diethyl dithiophosphoric acid in $CHCl_3$ at room temperature for 1 hr affording phenyl methyl sulfide (50%), O,O-diethyl-S-bis(carbomethoxy)methyl dithiophosphate (50%), phenyl bis(carbomethoxy)methyl sulfide (50%), and O,O-diethyl-S-methyl dithiophosphate (50%) (Eq. 6). In the case of diphenyl sulfonium bis(carbomethoxy)methylide the reaction with dithiophosphoric acid afforded diphenyl sulfide and O,O-diethyl-S-bis(carbomethoxy)methyl dithiophosphate (Eq. 7). When phenyl benzyl sulfonium bis(carbomethoxy)methylide was mixed with equimolar O,O-diethyl dithiophosphoric acid in $CHCl_3$ at room temperature, only phenyl bis(carbomethoxy)methyl sulfide and O,O-diethyl-S-benzyl dithiophosphate were obtained quantitatively (Eq. 8) apparently *via* S_N2 type attack of dithiophosphate anion on benzylic carbon.



$$\underset{\ominus C(CO_2Me)_2}{Ph-\overset{\oplus}{S}-Me} \xrightarrow{(EtO)_2PS_2H} \underset{(50\%)}{Ph-S-Me}, \quad \underset{(50\%)}{(EtO)_2PS_2CH(CO_2Me)_2} \quad \underset{(50\%)}{Ph-S-CH(CO_2Me)_2}, \quad \underset{(50\%)}{(EtO)_2PS_2Me} \qquad (6)$$



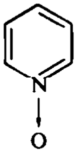
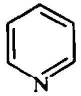
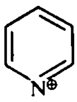
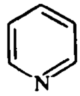
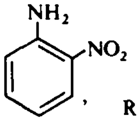
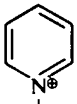
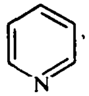
$$\underset{\ominus C(CO_2Me)_2}{Ph-\overset{\oplus}{S}-Ph} \xrightarrow{(EtO)_2PS_2H} Ph-S-Ph + (EtO)_2PS_2CH(CO_2Me)_2 \qquad (7)$$



$$\underset{\ominus C(CO_2Me)_2}{Ph-\overset{\oplus}{S}-CH_2Ph} \xrightarrow{(EtO)_2PS_2H} Ph-S-CH(CO_2Me)_2 + (EtO)_2PS_2CH_2Ph \qquad (8)$$

The reaction of pyridine N-*oxide and* N-*iminopyridinium betaines with* O,O-*diethyl dithiophosphoric acid.* Though tertiary amine N-oxides are known to be deoxygenated to the corresponding amine by trivalent phosphorus compounds[13] or dichlorocarbene,[14] a similar reaction of N-iminopyridinium betaines is not known. We have found that pyridine N-oxide was reduced to pyridine in 90% yield by heating with excess O,O-diethyl dithiophosphoric acid in refluxing $CHCl_3$ for 12 hr, while under the same conditions N-*o*-nitrophenyliminopyridinium betaine and N-benzoyliminopyridinium betaine were reduced to pyridine and *o*-nitroaniline, respectively (Table II).

TABLE II. THE REACTIONS OF PYRIDINE N-OXIDE AND N-IMINOPYRIDINIUM BETAINES WITH $(EtO)_2PS_2H$[a]

Substrate	Solvent	Reac. time (hr)	Product (yield %)
	$CHCl_3$	12	 (90%)
 $^{\ominus}$N—Ph—NO$_2$—o	$CHCl_3$	12	 (30%)  (30%) Recovered (70%)
 $^{\ominus}$N—CO—Ph	$CHCl_3$	12	 (30%) Recovered (70%)

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[a] All reactions proceed in refluxing $CHCl_3$ and bis[O,O-diethyl thiophosphoryl]disulfide, $[(EtO)_2PS]_2S_2$, was also obtained.

[b] Benzamide could not be isolated.

As will be described later, the reactions are considered to be nucleophilic substitutions on both the oxygen atom of N-oxide and the nitrogen atom of N-iminopyridinium betaine by O,O-diethyldithiophosphate anion.

The reaction of phosphine oxide, phosphine sulfide, and phosphine imine with O,O-*diethyl dithiophosphoric acid.* We have attempted the reduction of similar semi-polar compounds of phosphine, i.e. triphenylphosphine oxide, triphenylphosphine sulfide, and N-*p*-toluenesulfonyl triphenylphosphine imine with excess O,O-diethyl dithiophosphoric acid. However no reaction was found in refluxing $CHCl_3$ for 24 hr except in the case of triphenylphosphine oxide, in which a small amount of triphenylphosphine sulfide was formed. The P—O and even the P—S bond of these semipolar phosphorus compounds are so strong that they cannot be reduced by a weak reducing agent as dithiophosphoric acid. Only by use of strong reducing agents such as hexachlorodisilane[15] and trichlorosilane[16] can tetravalent phosphorous compounds be reduced to the corresponding trivalent compounds. Meanwhile, we have found that thioketones and thioaldehydes are formed by the reaction of ketones and aldehydes with dithiophosphoric acid.* Therefore, the formation of phosphine sulfide from phosphine oxide is considered to proceed by way of a similar process as in the case of ketones or aldehydes.

$$\mathrm{Ph_3P \rightarrow X \xrightarrow{\text{excess } (EtO)_2PS_2H} \text{no reduction}}$$

$$\mathrm{X = O, S, NTs}$$

DISCUSSION

The initial step of the deoxygenation of sulfoxides and sulfilimines by O,O-dialkyl dithiophosphoric acid is considered to be protonation either at the sulfoxide oxygen or the sulfilimine nitrogen, and subsequent nucleophilic attack of O,O-dialkyl dithiophosphate anion on the sulfur atom of the sulfoxide or the silfilimine would give a tetravalent intermediate, as postulated by Wallace *et al.*[12] Then reaction of the tetravalent intermediate with another O,O-dialkyl dithiophosphoric acid should give the final products (Chart 1). To give the final reaction products from this tetravalent intermediate, the central atom of group Y in Chart 1 must have a lone-pair. Sulfonium ylides however, do not have another lone-pair after the initial protonation of the ylide carbon atom. Therefore, even if a tetravalent intermediate was formed in the reaction between the sulfonium ylide and dithiophosphoric acid, the intermediate cannot give the reduction products by way of the same reaction scheme for sulfoxides and sulfilimines. A nucleophilic attack of O,O-diethyl dithiophosphate anion at the carbo-

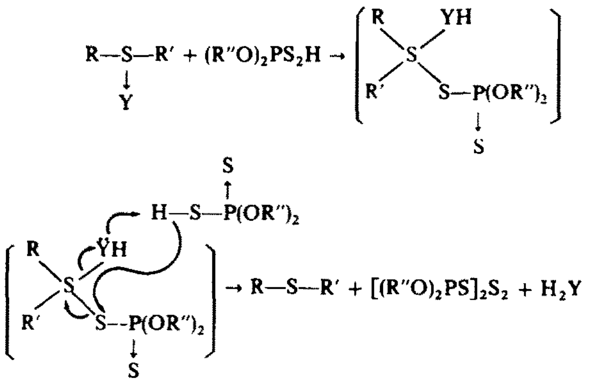

CHART 1

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* We shall report on this reaction in our forthcoming papers.

methoxymethyl carbon atom or another alkyl carbon atom attached to the sulfur atom would take place after the initial protonation at the carbon atom of the ylide. When R is either Ph or CH_2Ph, the reaction proceeds *via* two quite different processes (Chart 2). However, in the case of phenyl methyl sulfonium ylide it is assumed that O,O-diethyl dithiophosphate anion attacks both carbon atoms since steric effect and electronic effect are compensated.

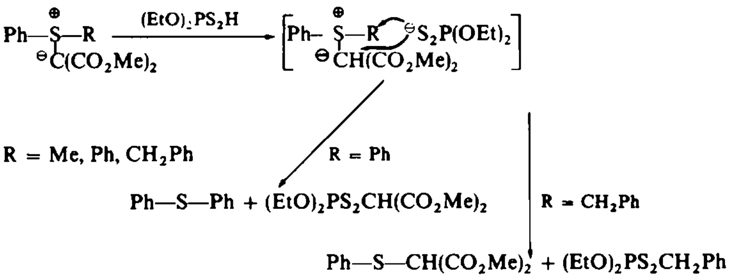

CHART 2

The successful reductions of pyridine N-oxide and N-iminopyridinium betaines to pyridine by dithiophosphoric acid are interesting since neither N-oxide nor betaine can form a pentavalent intermediate as can sulfoxides and sulfilimines. Therefore, the only plausible mechanistic route would involve nucleophilic attack of O,O-diethyl dithiophosphate anion on either the oxygen or the nitrogen atom, after initial protonation of either the oxygen atom of N-oxide or the nitrogen atom of N-iminopyridinium betaines (Chart 3). The resulting products, $(EtO)_2PS_2OH$, $(EtO)_2Ps_2NHCOPh$, and $(EtO)_2PS_2NHPh\text{-}NO_2\text{-}o$, are so unstable that they would react readily with another dithiophosphoric acid and give bis[O,O-diethyl thiophosphoryl]disulfide and other reduction products, i.e. *o*-nitroaniline. We have tried to obtain a similar intermediate, $(EtO)_2PS_2NH_2$, by treating hydroxylamine-O-sulfonic acid, generally an aminating agent,[17] with sodium O,O-diethyl dithiophosphate but only bis[O,O-diethyl thiophosphoryl]disulfide was obtained. Thus from the synthetic view point O,O-dialkyl dithiophosphoric acids are considered to be very useful reagents for reduction of compounds having somewhat weak semipolar bonds such as sulfoxides, sulfilimines, sulfonium ylides, tertiary amine N-oxides and N-iminopyridinium betaines, etc.

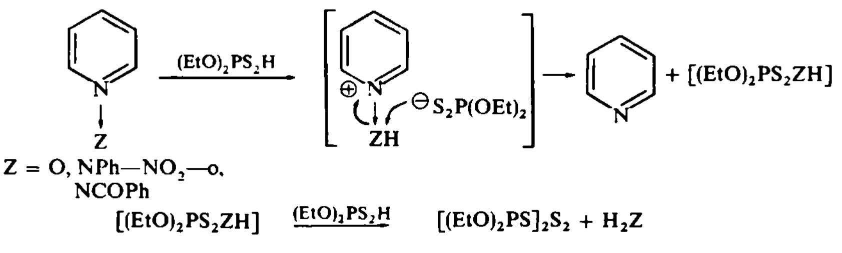

CHART 3

EXPERIMENTAL

NMR spectra were measured with a Hitachi–Perkin Elmer R-20 spectrometer (60 Mc) and IR spectra on Japan Spectroscopic, Co. Ltd. IR-G spectrometer. B.ps and m.ps are uncorrected.

O,O-*Dialkyl dithiophosphoric acids.* O,O-Dialkyl dithiophosphoric acids were prepared from P_2S_5 and the corresponding absolute alcohol according to the procedure reported by Kabacknik *et al.*[18] $(EtO)_2PS_2H$, b.p. 64–66°/2 mm (lit.[18] b.p. 81·5–82·5°/5 mm); $(i\text{-}PrO)_2PS_2H$, b.p. 71–72°/2 mm (lit.[18] b.p. 71–72°/3 mm).

Sulfoxides. The sulfoxides listed below were prepared by oxidation of the corresponding sulfides by Br_2 in the presence of pyridine in $AcOH/H_2O$, according to the usual procedure.[19] Phenyl methyl sulfoxide, b.p. 110°/1–2 mm (lit.[19] b.p. 84°/0·25 mm); phenyl ethyl sulfoxide, b.p. 101·5–102°/2 mm (lit.[20] b.p. 101–102°/1 mm); phenyl benzyl sulfoxide, m.p. 127° (lit.[21] m.p. 127°). Dimethyl sulfoxide was purified by repeated vacuum distillation of the commerical compound in the presence of NaH, b.p. 81–82°/20 mm (lit.[22] b.p. 86°/25 mm). Diphenyl sulfoxide was prepared by the reaction of $SOCl_2$, benzene, and $AlCl_3$, m.p. 70–71° (lit.[23] m.p. 71°).

N-p-*Toluenesulfonylsulfilimines.* All the N-*p*-toluenesulfonylsulfilimines were prepared from the reaction of the corresponding sulfides and chloramine T by the same procedure described previously.[24] Dimethyl N-*p*-toluenesulfonylsulfilimine, m.p. 157° (lit.[25] m.p. 157–157·5°); phenyl methyl N-*p*-toluenesulfonylsulfilimine, m.p. 129–130° (lit.[25] m.p. 129–130°); diphenyl N-*p*-toluenesulfonylsulfilimine, m.p. 112° (lit.[5] m.p. 111–112°).

Sulfonium bis(carbomethoxy)methylide. Sulfonium bis(carbomethoxy)methylide were synthesized according to the procedure reported earlier by Ando *et al.*[26] Phenyl methyl sulfonium bis(carbomethoxy)methylide, m.p. 125–126° (lit.[26] m.p. 126–127°); diphenyl sulfonium bis(carbomethoxy)methylide, m.p. 128° lit.[26] m.p. 127–128°); phenyl benzyl sulfonium bis(carbomethoxy)methylide, m.p. 150·5° (lit.[27] m.p. 150·5–151·0°).

Pyridine N-*oxide.* This amine N-oxide was obtained by the oxidation of pyridine in AcOH and 30% H_2O_2 aq according to Ochiai,[28] b.p. 104–105°/2 mm (lit.[29] b.p. 130–131°/9 mm).

N-*Iminopyridinium betaines.* Betaines were prepared according to Tamura *et al.*[30] N-*o*-nitrophenyliminopyridinium betaine, m.p. 147–148° (lit.[30] m.p. 147–148°); N-benzoyliminopyridinium betaine, m.p. 229° (lit.[30] m.p. 229°).

Triphenylphosphine oxide. Triphenylphosphine oxide was purified by recrystallization of commercial product from EtOH, m.p. 155–156° (lit.[31] m.p. 156°).

Triphenylphosphine sulfide. Triphenylphosphine sulfide was prepared by reaction of commercial triphenylphosphine with sulfur according to Bartlett *et al.*,[32] m.p. 160–161° (lit.[32] m.p. 161°).

N-p-*Toluenesulfonyl triphenylphosphine imine.* This phosphine imine was prepared by the method developed in our laboratory,[6a] m.p. 192–194° (lit.[33] m.p. 193–194°).

Thiophenol was purified by vacuum distillation of commercial material, b.p. 70–72°/5 mm (lit.[34] b.p. 71°/15 mm).

Reaction of dimethyl sulfoxide with thiophenol. DMSO (2 g) and thiophenol (6 g) were heated at 80° for 12 hr. Dimethyl sulfide evolved and was trapped in a cooled vessel, b.p. 37°/760 mm (lit.[22] b.p. 38°/760 mm). When the reaction mixture cooled diphenyl disulfide crystallized. After recrystallization 5·1 g of disulfide was obtained, m.p. 60–61° (lit.[35] m.p. 60–61°).

General procedure for the reaction of sulfoxides and sulfilimines with O,O-*dialkyl dithiophosphoric acid.* After sulfoxides or sulfilimines (1 mole) were reacted with O,O-dialkyl dithiophosphoric acid (2 mole) either in $CHCl_3$ or neat, the products were isolated by column chromatography (silica-gel column, benzene–hexane). Sulfides and bis[O,O-dialkyl thiophosphoryl]disulfides[36] were identified by comparing physical properties with those of authentic samples.

Reaction of phenyl methyl sulfoxide with O,O-*diethyl dithiophosphoric acid.* When O,O-diethyl dithiophosphoric acid (4 g) was added to 1·4 g of phenyl methyl sulfoxide vigorous exothermic reaction suddenly occurred. The mixture was kept standing at room temp, and chromatographed through a silica-gel column with benzene-hexane giving 1·2 g of phenyl methyl sulfide and 3·5 g of bis[O,O-diethyl thiophosphoryl]disulfide.

Reaction of N-p-*toluenesulfonyl phenyl methyl sulfilimine with* O,O-*diethyl dithiophosphoric acid.* As soon as O,O-diethyl dithiophosphoric acid (4 g) was added to 2·93 g of N-*p*-toluenesulfonyl phenyl methyl sulfilimine, *p*-toluenesulfonamide precipitated with evolution of heat. After a small amount of n-hexane was added to the mixture, *p*-toluenesulfonamide was filtered. The filtrate was treated similarly, and *p*-toluenesulfonamide (1·6 g), m.p. 134–135° (lit.[37] m.p. 137·5°), 1·1 g of phenyl methyl sulfide and 3·6 g of bis[O,O-diethyl thiophosphoryl]disulfide were obtained.

Reaction of phenyl methyl sulfonium bis(carbomethoxy)methylide with O,O-diethyl dithiophosphoric acid. To a $CHCl_3$ solution containing 2·5 g phenyl methyl sulfonium bis(carbomethoxy)methylide 1·9 g of O,O-diethyl dithiophosphoric acid was added, and the mixture kept at room temp for 1 hr. Through silica-gel column chromatography first benzene eluted 0·6 g of phenyl methyl sulfide, and then 1 g of O,O-diethyl-S-methyl dithiophosphate, and a mixture of phenyl bis(carbomethoxy)methyl sulfide (2·7 g) and O,O-diethyl-S-bis(carbomethoxy)methyl dithiophosphate. The latter mixture could not be separated by TLC but only by GLC (high vacuum silicone grease). These two products were identified by comparing their GLC retention times and NMR spectra with those of authentic samples, and the product ratio determined by comparing the integration intensities of the phenyl protons of phenyl bis(carbomethoxy)methyl sulfide and the methyl protons of O,O-diethyl-S-bis(carbomethoxy)methyl dithiophosphate.

Reaction of diphenyl sulfonium bis(carbomethoxy)methylide with O,O-diethyl dithiophosphoric acid. To a $CHCl_3$ solution containing 3·16 g diphenyl sulfonium bis(cabomethoxy)methylide 1·86 g of O,O-diethyl dithiophosphoric acid was added. After the mixture was kept at room temp for 1 hr, it was treated as for phenyl methyl sulfonium bis(carbomethoxy)methylide giving quantitatively diphenyl sulfide and O,O-diethyl-S-bis(carbomethoxy)methyl dithiophosphate.

Reaction of phenyl benzyl sulfonium bis(carbomethoxy)methylide with O,O-diethyl dithiophosphoric acid. To a $CHCl_3$ solution containing 3·3 g of phenyl benzyl sulfonium bis(carbomethoxy)methylide, 1·86 g of O,O-diethyl dithiophosphoric acid was added. The mixture was kept at room temp for 1 hr and treated as for phenyl methyl sulfonium ylide giving quantitatively phenyl bis(carbomethoxy)methyl sulfide and O,O-diethyl-S-benzyl dithiophosphate.

Preparation of the authentic samples formed by the reaction of sulfonium ylide with O,O-diethyl dithiophosphoric acid. $(EtO)_2PS_2CH(CO_2Me)_2$ was prepared by the reaction of $(EtO)_2PS_2H$ with $BrCH(CO_2Me)_2$ in the presence of Et_3N in benzene.

$(EtO)_2PS_2Me$ and $(EtO)_2PS_2CH_2Ph$ were prepared from $(EtO)_2PS_2H$ and the corresponding halides in the presence of Et_3N in benzene.

$PhSCH(CO_2Me)_2$ was prepared by the reaction between $CH_2(CO_2Me)_2$ and $PhSNEt_2$ according to the procedure reported by Mukaiyama *et al.*[38]

TABLE III. NMR SPECTRA OF THESE AUTHENTIC SAMPLES IN CCl_4 FROM EXTERNAL TMS

Comp.	Chemical Shift (ppm)
$(EtO)_2PS_2CH(CO_2Me)_2$	1·4 (t, 6H, J_{CHCH} 7 Hz), 3·8 (s, 6H), 4·2 (q, d, 4H, J_{CHCH} 7 Hz, J_{POCH} 11 Hz), 4·55 (d, 1H, J_{PSCH} 16 Hz)
$(EtO)_2PS_2Me$	1·4 (t, 6H, J_{CHCH} 7 Hz), 2·3 (d, 3H, J_{PSCH} 16 Hz), 4·15 (q, d, 4H, J_{CHCH} 7 Hz, J_{POCH} 11 Hz)
$(EtO)_2PS_2CH_2Ph$	1·35 (t, 6H, J_{CHCH} 7 Hz), 4·0 (d, 2H, J_{PSCH} 16 Hz), 4·15 (q, d, 4H, J_{CHCH} 7 Hz, J_{POCH} 11 Hz), 7·4 (m, 5H)
$PhSCH(CO_2Me)_2$	3·7 (s, 6H), 4·45 (s, 1H), 7·4 (m, 5H)

Reaction of pyridine N-*oxide with O,O-diethyl dithiophosphoric acid.* After a $CHCl_3$ solution containing 0·95 g of pyridine N-oxide and 7·4 g of O,O-diethyl dithiophosphoric acid was heated under reflux for 12 hr, the mixture was neutralized with solid Na_2CO_3, extracted with conc. HCl solution, water was evaporated in vacuo and the residue treated with an ethanolic picric acid to give 2·77 g of pyridine picrate, m.p. 161–163° (lit.[39] m.p. 165°).

Reaction of N-*o*-*nitrophenyliminopyridinium betaine with O,O-diethyl dithiophosphoric acid.* To a solution containing N-*o*-nitrophenyliminopyridinium betaine (2·15 g) in $CHCl_3$ was added dropwise a $CHCl_3$ solution of O,O-diethyl dithiophosphoric acid (7·4 g). After the mixture was refluxed for 12 hr, excess solid Na_2CO_3 was added and the mixture neutralized. Half of the $CHCl_3$ solution was concentrated in vacuo at 60°, and the residue chromatographed through a silica-gel column with $CHCl_3$ to give bis[O,O-diethyl thiophosphoryl]disulfide, 21 mg of *o*-nitroaniline and 750 mg of recovered N-*o*-nitroiminopyridinium betaine. The other $CHCl_3$ solution was extracted with conc. HCl, and water evaporated. The residue was treated with ethanolic picric acid to give the picrate of the mixture of pyridine and N-*o*-nitrophenyliminopyridinium betaine (1·95 g). Yield of pyridine was determined as 30% from this experimental result.

Reaction of N-*benzoyliminopyridinium betaine with* O,O-*diethyl dithiophosphoric acid.* A $CHCl_3$ solution containing N-benzoyliminopyridinium betaine (1·98 g) and O,O-diethyl dithiophosphoric acid (7·4 g) was refluxed for 12 hr, and excess solid Na_2CO_3 added to neutralize the mixture. The $CHCl_3$ solution was extracted with conc. HCl, and the organic layer dried ($MgSO_4$) and concentrated *in vacuo* to yield bis[O,O-diethyl thiophosphoryl]disulfide. Otherwise, the aqueous layer was concentrated under reduced pressure to give crude white crystals, containing HCl salts of pyridine and N-benzoyliminopyridinium betaine. Half of the crude white crystals were treated with ethanolic picric acid to give a picrate of pyridine and N-benzoyliminopyridinium betaine (1·96 g). To the other half a small amount of water was added, neutralized with aqueous Na_2CO_3, and extracted with $CHCl_3$, dried ($MgSO_4$) and $CHCl_3$ removal *in vacuo* at 60°, gave 690 mg of N-benzoyl-iminopyridinium betaine. Yield of pyridine was 30% based on experimental data.

Reactions of triphenylphosphine oxide, triphenylphosphine sulfide, and N-p-*toluenesulfonyl triphenylphosphine imine with* O,O-*diethyl dithiophosphoric acid.* A $CHCl_3$ solution containing either one of these three substrates (1 mole) and O,O-diethyl dithiophosphoric acid (4 mole) was refluxed for 24 hr, and then neutralized with solid Na_2CO_3. $CHCl_3$ was evaporated under reduced pressure to give residue found to be starting material in three cases. Only in the reaction of triphenylphosphine oxide with O,O-diethyl dithiophosphoric acid was a minute amount of triphenylphosphine sulfide identified by TLC.

*Reaction between hydroxylamine-*O-*sulfonic acid and* O,O-*diethyl dithiophosphoric acid.* To alcohol solution of sodium hydroxylamine-O-sulfonate[40] (0·01 mole) was added an alcohol solution of sodium O,O-diethyl dithiophosphate (0·1 mole). After an hour a small amount of water was added and the mixture $CHCl_3$ extracted, dried ($MgSO_4$) and $CHCl_3$ removed to give quantitatively bis[O,O-diethyl thiophosphoryl]disulfide.

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