phosphine (infrared spectrum and mixture melting point with an authentic sample). Further elution with benzene gave 1.3 g of *cis*-N-cinnamyl-*p*-toluenesulfonanilide. Based on a 53% conversion (0.0119 moles reacted) of the benzaldehyde, the total yields are 14% triphenylphosphine, 47% triphenylphosphine oxide, and 30% *cis*-N-cinnamyl-*p*-toluenesulfonanilide. Recrystallization of the *cis*-N-cinnamyl-*p*-toluenesulfonanilide from methanol gave analytically pure, white crystals, mp 83.5–84.0°.

Anal. Calcd for $C_{22}H_{21}NO_2S$: C, 72.71; H, 5.82; N, 3.85. Found: C, 72.76; H, 5.82; N, 4.01.

The nmr spectrum in deuteriochloroform showed a singlet at 2.31 ppm, wt 3.0 ($ArCH_3$); a split doublet centered at 4.46 ppm, wt 2.1 (CCH_2N); a multiplet centered at 5.63 ppm, wt 0.84 ($ArCH{=}CH$); a doublet at 6.47 ppm, wt 0.84 ($ArCH{=}CH$); and a multiplet ranging from 6.9 to 7.6 ppm, wt 14.4 (aryl protons). The infrared spectrum showed a weak–medium C=C stretching band at 1600 cm^{-1} and only very weak bands in the 960–990-cm^{-1} *trans* absorption region.

Phenyl *trans*-Cinnamyl Sulfide.—Sodium hydride (0.05 mole) was allowed to react with 150 ml of thiophenol. After 14 hr 0.05 mole of vinyl triphenylphosphonium bromide and 0.05 mole of benzaldehyde were added and the temperature was held at 90° for 4 days. Ether and water were added and ether extraction was carried out. The ether layer was washed well with 2 *N* NaOH and with water and dried over magnesium sulfate. Evaporation of the ether solution gave a solid to which was added dry ethanol. From this solution was recrystallized 7.7 g (68%) of the phenyl cinnamyl sulfide, mp 77–77.5° (lit.[18] mp 78°). Vapor phase chromatograph indicated only one peak, shown by infrared and nmr analysis to be the *trans* isomer.

The nmr spectrum in CCl_4 showed a doublet at 3.6 ppm, wt 1.9 (SCH_2); a multiplet from 6.1 to 6.6 ppm, wt 1.9 (vinyl protons); and a singlet at 7.33 ppm, wt 10.0 (aryl protons). The infrared spectrum showed a medium–strong C=C stretch at 1580 cm^{-1} and a strong *trans* hydrogen band at 965 cm^{-1}.

Diethyl Ethyl(2-cyclohexylideneethyl)malonate.—Sodium hydride (0.06 mole) was allowed to react with 0.06 mole of diethyl ethylmalonate in 100 ml of anhydrous ether. At the completion of the reaction, the ether was distilled off and 350 ml of dimethylformamide was added, followed by addition of 0.06 mole of cyclohexanone and 0.061 mole of vinyltriphenylphosphonium bromide. The reaction mixture was held at 90–100° for 8 days. Ether and water were added and ether extraction was carried out. The dry ether extracts were distilled to give a 14% yield of diethyl ethyl(2-cyclohexylideneethyl)malonate, bp 134–135° (0.9 mm), $n^{25}D$ 1.4714 [lit.[19] bp 152–153° (3 mm)].

The nmr spectrum in CCl_4 showed a complex multiplet centered at 4.1 ppm, wt 4.8 (assigned to the four protons from the methylene groups adjacent to the oxygen in the ester linkage, and to the one proton on the double bond); and a complex multiplet ranging from 0.61 to 2.42 ppm, wt 23.2 (assigned to all other hydrogens in the molecule). The infrared spectrum showed a medium C=C stretch at 1600 cm^{-1}, a strong C=O stretch at 1740 cm^{-1}, and was otherwise in accordance with the structure assigned.

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The Constitution of Crude O,O-Dimethyl- and O,O-Diethyldithiophosphoric Acids Prepared from Phosphorus Pentasulfide

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The chief constituents of the neutral fraction of crude O,O-dimethyl- and O,O-diethyldithiophosphoric acids were characterized; all but one of these were shown to be convertible to the corresponding phosphorochloridothioate on chlorination.

The neutral fraction of crude O,O-diethyldithiophosphoric acid, obtained from phosphorus pentasulfide and ethanol, was investigated by Bacon and LeSuer[1] and by McIvor, *et al.*[2] The former authors obtained triethyl phosphorothionate and O,O,O,O-tetraethyl trithiopyrophosphate, together with elemental sulfur, by fractional distillation. The latter authors reported O,O,S-triethyl phosphorodithioate and S,S-bis(diethylphosphorothionyl)-O-ethyl phosphorothionate by a similar treatment, and state that O,O,S-trimethyl phosphorodithioate was obtained from the reaction of methanol with phosphorus pentasulfide.

With the availability of the nmr analytical method, it became of interest to reinvestigate the neutral fraction of crude methyl and ethyl phosphorodithioates, with a view particularly to determining which constituents are convertible to phosphorochloridothioates on chlorination. Table I shows the nmr peaks found in the neutral fractions of crude methyl and ethyl phosphorodithioic acids, together with the approximate percentage range found in different samples and the structure assignments made.

The structure assignments were made on the following basis.

Methyl Series.—Vacuum distillation of the neutral fraction derived by conventional methods[1,2] from crude O,O-dimethylphosphorodithioic acid gave a distillate showing identical nmr peaks at −88.0- and −60.2-ppm shift, together with a minor peak at −73.0 ppm. Refractionation gave an analytical sample [bp 84° (56 mm), $n^{23}D$ 1.4772] with nmr peaks as above, less that at −73.0 ppm. The two peaks were 655 cps apart, each split into seven parts (14.1 cps). On H^1 decoupling, they fused to a single peak at −74.1-ppm shift. Physical constants (other than nmr) are in good agreement with reported values[3] for O,O-dimethyl hydrogen phosphonothioate.

The peak at −73.4 ppm was assigned to trimethyl phosphorothionate on the basis of the nmr spectrum, which had identical shift and splitting with that shown by an authentic specimen.

The peak at −89.0 ppm was assigned to the disulfide structure $[(CH_3O)_2PS]_2S_2$ on the basis of its chemical shift, which was the same as that shown by an authentic specimen prepared from O,O-dimethyl phosphorodi-

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(1) W. E. Bacon and W. M. LeSuer, *J. Am. Chem. Soc.*, **76**, 670 (1954).

(2) R. A. McIvor, G. D. McCarthy, and G. A. Grant, *Can. J. Chem.*, **34**, 1819 (1956).

(3) M. I. Kabachnik and T. A. Mastryukova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 727 (1952).

TABLE I

NMR PEAKS OF THE NEUTRAL FRACTION OF CRUDE O,O-DIMETHYL- AND DIETHYLPHOSPHORODITHIOATES[a]

Methyl			Ethyl		
Chemical shift[a]	%	Structure	Chemical shift[a]	%	Structure
−99.6	6–20	$(CH_3O)_2PSSCH_3$	−94.1	<2	$(C_2H_5O)_2PSSC_2H_5$
−89.0	21–58	$[(CH_3O)_2PS]_2S_2$	−84.0	19	$[(C_2H_5O)_2PS]_2S_2$
		$(CH_3O)_2PSH$	−81.5	2	$(C_2H_5O)_2PSH$
−83.5	27–37	$[(CH_3O)_2PS]_2S$	−78.0	63	$[(C_2H_5O)_2PS]_2S$
−73.4	3–9	$(CH_3O)_3PS$	−76.1	2	Unassigned
−60.9	7–16	$(CH_3O)_2PSH$	−67.6	6	$(C_2H_5O)_3PS$
−56.2	0–11	Unassigned	−55.3	2	$(C_2H_5O)_2PSH$
			−52.4	2	Unassigned

[a] In parts per million relative to 85% H_3PO_4.

thioic acid by oxidation with hydrogen peroxide. It overlaps one of the peaks due to O,O-dimethyl hydrogen phosphonothioate.

The peak at −83.5 ppm is the same as that of O,O,-O,O-tetramethyltrithiopyrophosphate prepared according to Mel'nikov, *et al.*[4]

The peak at −99.6 ppm was assigned to O,O,S-trimethyl phosphorodithioate by comparison with the nmr spectrum of an authentic specimen prepared by methylation of O,O-dimethyl phosphorodithioic acid. This confirms the findings of McIvor, *et al.*,[2] who obtained this compound also from methanol and P_4S_7.

Ethyl Series.—The neutral fraction of crude O,O-diethyl phosphorodithioic acid occasionally deposits crystals on standing. A sample of these, after several recrystallizations, had mp 41°, and proved to be identical with O,O,O,O-tetraethyl trithiopyrophosphate prepared according to Mel'nikov, *et al.*[4] Its nmr shift shows it to be responsible for the peak at −78.0 ppm present in the nmr spectrum of the neutral fraction. The volatile portion of the ethyl neutral fraction had a nmr spectrum showing identical peaks at −82.3 and −55.5 ppm., each split into five parts, the mean of which corresponds with the shift of −69.0 ppm reported by Finegold[5] for O,O-diethyl hydrogen phosphonothioate. This identifies the corresponding two peaks reported in Table I. The same compound was reported by McIvor[2] to be formed from ethanol and P_4S_7.

The nmr spectrum of the volatile portion also showed a peak at −67.6 ppm split into seven parts, identical with that of an authentic specimen of triethyl phosphorothionate, and a minor peak at −94.1 ppm assigned to O,O,S-triethyl phosphorodithioate by comparison with an authentic sample prepared from O,O-diethyl phosphorochloridothioate and O,O-diethyl phosphorodithioic acid in the presence of base. This latter reaction must proceed by the following scheme, which was found to apply in both the methyl and ethyl series.

$$(RO)_2PSCl + BH^+(RO)_2PSS^- \longrightarrow (RO)_2PSSR + BHCl + [ROP(O)S]_x$$

This reaction is believed to be closely similar to that reported by Meinhardt and Vogel[6] for the interaction between O,O-dialkylphosphorodithioic acids and their amine salts. The report by Malatesta[7] that O,O,O,O-tetraethyl trithiopyrophosphate is formed in this reaction could not be substantiated.

The nmr peak at −84.0 ppm was assigned to the disulfide structure, $[(C_2H_5O)_2PS]_2S_2$, on the basis of its identity with that of an authentic specimen prepared by oxidation of O,O-diethylphosphorodithioic acid with hydrogen peroxide.

No evidence could be found for the presence of the product of mp 47° reported by McIvor, *et al.*,[2] as a constituent of the neutral fraction of crude O,O-diethylphosphorodithioic acid, and to which they ascribed the S,S-bis(diethyl phosphorothionyl)-O-ethyl phosphorothionate structure. It is believed that these authors were dealing with O,O,O,O-tetraethyl trithiopyrophosphate, though this was found to melt at 41° by Bacon and LeSuer,[1] Mel'nikov, *et al.*,[4] and by ourselves.

Elemental sulfur was also present in both ethyl and methyl neutral fractions. The structure assignments made in each series are closely parallel, and corroborate one another. Further confirmation was obtained by chlorinating the respective neutral fractions. It was found that all nmr peaks assigned, except that due to $(RO)_3PS$, disappear on chlorination in favor mainly of a peak characteristic of the corresponding dialkyl phosphorochloridothioate, which was isolated from the product. This is in agreement with the assigned structures, as the formation of this compound by chlorination of the disulfide $[(RO)_2PS]_2S_2$ has been described by Hechenbleikner[8] and by Yamasaki;[9] chlorination of diethyl hydrogen phosphonothioate to the phosphorochloridothioate was reported by Kabachnik and Mastryukova.[10] The conversion of O,O,S-trimethyl and O,O,S-triethyl phosphorodithioates into the corresponding phosphorochloridothioates was shown on synthetic samples by nmr analysis.

Experimental Section[11]

Oxidation of O,O-Dimethylphosphorodithioic Acid to the Disulfide.—The acid (100 g) was treated with 1000 ml of ice–water and 43 ml of 30% hydrogen peroxide for 0.5 hr at 5–10°. The product was stirred for 2 hr longer, after which it was filtered to give 62 g of colorless crystals of mp 52° after recrystallization from methanol. Kabachnik and Mastryukova[12] reported mp

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(4) N. N. Mel'nikov, K. D. Shvetsova-Shilovskaya, and M. Ya. Kagan, *Zh. Obshch. Khim.*, **30**, 2319 (1960).

(5) H. Finegold, *Ann. N. Y. Acad. Sci.*, **70**, 875 (1958).

(6) N. A. Meinhardt and P. W. Vogel, *J. Org. Chem.*, **24**, 1604 (1959).

(7) L. Malatesta, *Gazz. Chim. Ital.*, **81**, 596 (1951).

(8) I. Hechenbleikner, U. S. Patent 2,482,063 (1949).

(9) T. Yamasaki, *Sci. Rept. Res. Inst., Tohuku Univ.*, **A4**, 403 (1952).

(10) M. I. Kabachnik and T. A. Mastryukova, *Bull. Acad. Sci. USSR*, 145 (1953).

(11) All P^{31} nmr data were obtained at 24.3 Mc/sec and are referred to 85% H_3PO_4.

(12) M. I. Kabachnik and T. A. Mastryukova, *Bull. Acad. Sci. USSR*, 121 (1953).

51–52° for this product. The P^{31} nmr shift was found to be −88.3 ppm, with the expected split into seven parts.

After standing for 1 month in a glass bottle, the product had formed two liquid layers. Nmr analysis showed that extensive decomposition had taken place.

Oxidation of O,O-Diethylphosphorodithioic Acid to the Disulfide.—The acid (97.5 g) was treated as above with 30 ml of hydrogen peroxide. After allowing to stand overnight, the product was extracted with methylene chloride, dried with sodium sulfate, and stripped of solvent, giving 86 g of the liquid disulfide. This was found to have a P^{31} nmr shift of −83.7 ppm. After standing 7 months, a sample was found by repeated nmr analysis to have almost entirely decomposed.

O,O,O,O-Tetraethyl Trithiopyrophosphate.—The disulfide from ethyl thio acid (20 g), in 75 ml of benzene, was treated with 14 ml of triphenyl phosphite. After heating 1 hr at 60°, the solvent was removed *in vacuo*. The crude product showed P^{31} nmr peaks at −78.4 {$[(C_2H_5O)_2PS]_2S$} and −52.9 ppm $[(C_6H_5O)_3PS]$, together with a small peak at −128 ppm due to excess triphenyl phosphite. Attempted distillation at 0.15 mm led to decomposition, and separation of the product from triphenyl thiophosphate was finally accomplished by a lengthy series of crystallizations from hexane and methanol. The pure material had mp 42.5–43°, undepressed by admixture with a sample isolated from the ethyl neutral fraction. The infrared and H^1 nmr spectra of the two samples were identical.

O,O,O,O-Tetramethyl Trithiopyrophosphate.—This product was prepared as above from the disulfide of methyl thio acid and triphenyl phosphite, which led to a mixture of it with triphenyl thiophosphate. This proved to be undistillable in our hands, nor could it be separated by chromatography or by fractional crystallization. P^{31} nmr analysis of the crude product showed the desired compound to have a chemical shift of −83.5 ppm.

An attempt at substituting potassium cyanide for triphenyl phosphite failed to lead to the simple sulfur disproportionation reaction.

O,O,S-Trimethyl Phosphorodithioate. A. By Methylation of O,O-Dimethylphosphorodithioic Acid.—The acid (1 g) in 25 ml of dry ether was treated with diazomethane in 200 ml of dry ether prepared from 2 g of N-methyl-N-nitroso-N-nitroguanidine at room temperature. The ether solution was washed with water, dried over sodium sulfate, and evaporated. The residual yellow oil weighed 1 g, $n^{26}D$ 1.5273; the P^{31} nmr spectrum showed ten peaks at −99.5 ppm with a P–H splitting constant of 15.3 cps.

B. By Reaction of O,O-Dimethylphosphorodithioic Acid with O,O-Dimethyl Phosphorochloridothioate.—The thio acid chloride (17 g) was added to a mixture of the thio acid (17.6 g) with triethylamine (20 g) in 100 ml of benzene over 0.5 hr at 50–55°. After stirring 0.5 hr longer, the product was washed with dilute sodium hydroxide and water until neutral. After drying and stripping off the solvent, the product was distilled, yielding 2.2 g of a fraction of bp 55° (2 mm), $n^{25}D$ 1.5273 [lit. bp 51–52° (0.2 mm),[13] 101–101.5° (16.5 mm);[3] $n^{20}D$ 1.5200,[13] 1.5292[3]]; infrared and P^{31} and H^1 nmr spectra identical with those of the sample previously obtained.

Anal. Calcd for $C_3H_9PS_2O_2$: C, 20.92; H, 5.26; P, 18.00; S, 37.22. Found: C, 20.48; H, 5.46; P, 18.35; S, 37.74.

O,O,S-Triethyl Phosphorodithioate.—O,O-Diethylphosphorodithioic acid (19 g) was treated in 100 ml of benzene with 20 g of triethylamine and 19 g of O,O-diethyl phosphorochloridothioate, the mixture was refluxed 1 hr, cooled, and filtered. The filtrate deposited a viscous oil, which contained 14.43% S and 4.31% N.

TABLE II

COMPOSITION OF THE METHYL THIO ACID NEUTRAL FRACTION BEFORE AND AFTER CHLORINATION

P^{31} nmr chemical shift, ppm	Before chlorination, mole %	After chlorination, mole %	Structure assignment
−99	6	. .	$(CH_3O)_2PSSCH_3$
−89	36	6	$[(CH_3O)_2PS]_2S_2$ $(CH_3O)_2PSH$
−83	32	. .	$[(CH_3O)_2PS]_2S$
−73	3	73	$(CH_3O)_3PS$ (unchlorinated) $(CH_3O)_2PSCl$ (chlorinated)
−56	7	8	Unassigned
−61	16	. .	$(CH_3O)_2PSH$

TABLE III

COMPOSITION OF THE ETHYL THIO ACID NEUTRAL FRACTION BEFORE AND AFTER CHLORINATION

P^{31} nmr chemical shift, ppm	Before chlorination, mole %	After chlorination, mole %	Structure assignment
−84	19	24	$[(C_2H_5O)_2PS]_2S_2$
−78	63	. .	$[(C_2H_5O)_2PS]_2S$
−76	7	. .	Unassigned
−68	6	71	$(C_2H_5O)_3PS$ (unchlorinated) $(C_2H_5O)_2PSCl$ (chlorinated)

The benzene solution (top layer) was stripped of solvent and distilled twice *in vacuo*, yielding 12 g of product of bp 81–82° (2 mm), $n^{28}D$ 1.5008. The P^{31} nmr spectrum showed 14 peaks at −94.1 ppm; H^1 nmr and infrared spectra were in agreement with the assigned structure.

Anal. Calcd for $C_6H_{15}O_2PS_2$: C, 33.63; H, 7.06; P, 14.46; S, 29.9. Found: C, 32.58; H, 6.58; P, 15.05; S, 31.9.

These physical constants are in good agreement with those reported for this compound by Meinhardt and Vogel,[6] Kabachnik and Mastryukova,[3] and Mel'nikov, *et al.*[13]

Chlorination of O,O,S-Trimethyl and Triethyl Phosphorodithioates.—O,O,S-Trimethyl phosphorodithioate (1.45 g) was dissolved in 25 ml of methylene chloride and treated at 0° with a solution of 0.6 g of chlorine in the same solvent. Evaporation to dryness gave 1.7 g of a yellow oil of unpleasant odor, which showed the P^{31} nmr peak at −72.4 ppm, characteristic of O,O-dimethyl phosphorochloridothioate.

O,O,S-Triethyl phosphorodithioate, when treated as above, resulted in a product showing the P^{31} nmr peak at −67.7 ppm, characteristic of O,O-diethyl phosphorochloridothioate.

Chlorination of the Neutral Fraction of Crude Methyl and Ethyl Thio Acids.—The neutral fractions from crude O,O-dimethyl- and O,O-diethylphosphorodithioic acid were dissolved in 150 ml of methylene chloride and treated with 1 equiv of chlorine dissolved in the same solvent, at room temperature. Analysis of the product before and after chlorination by P^{31} nmr spectroscopy showed the composition reported in Tables II and III. Distillation of the chlorinated product gave 50% yield of material of bp 73–74° (23 mm), $n^{25.5}D$ 1.4774, identified as O,O-dimethyl phosphorochloridothioate.

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[13] N. N. Mel'nikov, K. D. Shvetsova-Shilovskaya, and M. Ya. Kagan, *Zh. Obshch. Khim.*, **30**, 200 (1960).