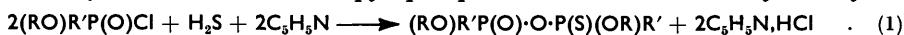


714. *The Structure of Dialkylthiopyrophosphonates and Related Compounds.*

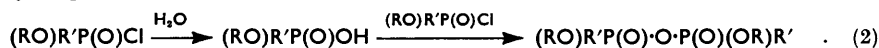
By D. G. COE, B. J. PERRY, and R. K. BROWN.

Dialkyl dialkylthiopyrophosphonates have been prepared by the action of hydrogen sulphide and pyridine on alkyl alkylphosphonochloridates. The infrared spectra of these compounds indicate a thiono-structure as does that of the analogous tetraethyl thiopyrophosphate. Tetraethyl selenopyrophosphate also exhibits a selenono-structure.

ORGANIC pyrophosphates are now of considerable interest as potential insecticides and the possibility of improving their insecticidal properties by incorporation of a sulphur atom has led to the synthesis of several thiopyrophosphates.¹ A series of dialkyl dialkylthio-



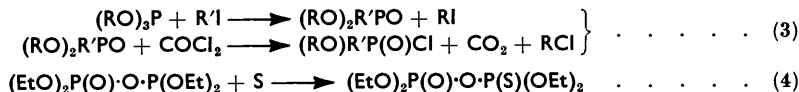
pyrophosphonates has now been prepared from the appropriate alkyl alkylphosphonochloridate essentially by the procedure used by Fiszer *et al.*¹ for the preparation of thiopyrophosphates. The analogous dialkyl dialkylpyrophosphonates were also prepared, by the action of water on the alkyl alkylphosphonochloridates, pyridine being used to remove hydrogen chloride :



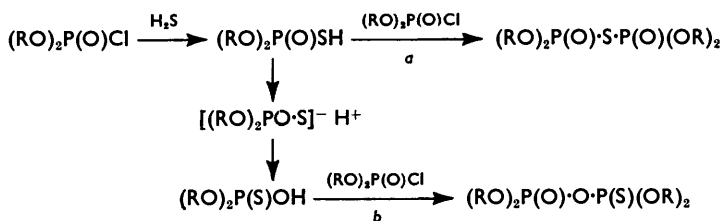
¹ Fiszer, Michalski, and Wiczorkowski, *Roczniki Chem.*, 1953, **27**, 482; Kosolapoff, U.S.P., 2,582,204 and 2,567,154/1951; Harman and Stiles, U.S.P. 2,630,450/1953; Schrader and Muhlman, G.P. 848,812/1952; Arbusov, Alinsov, Zvereva, Neklesova, and Kudrina, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1954, 1038.

Tetraethyl thiopyrophosphate was prepared by two routes—the “hydrogen sulphide method” (Fiszer *et al.*¹), and from diethyl phosphite and sulphur monochloride in presence of pyridine (Harman and Stiles¹). The products were identical. Tetraethyl selenopyrophosphate was prepared by Michalski and Wiczorkowski’s method.²

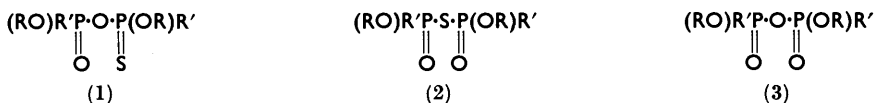
The phosphonochloridates were prepared from dialkyl alkylphosphonates by Arbusov’s method followed by treatment with carbonyl chloride :³



On the basis of the synthetical route (4) used, Arbusov and Arbusov⁴ assigned to tetraethyl thiopyrophosphate the thiono-structure shown. Most subsequent workers¹ have assumed this to be correct although the synthesis was often ambiguous. Fiszer *et al.*¹ considered that their “hydrogen sulphide” route would lead more logically to the bis(dialkoxyphosphinyl) sulphide structure as in route (a). However, the ionic nature of the dialkyl hydrogen phosphorothiolate would permit reaction in either form. The same considerations apply to the similar synthesis of the dialkylthiopyrophosphonates, and are equally applicable in a reverse sense if a sodium phosphorothionate (or selenonate) is used as an intermediate. In order to elucidate the structure of these compounds their infrared spectra have been examined.



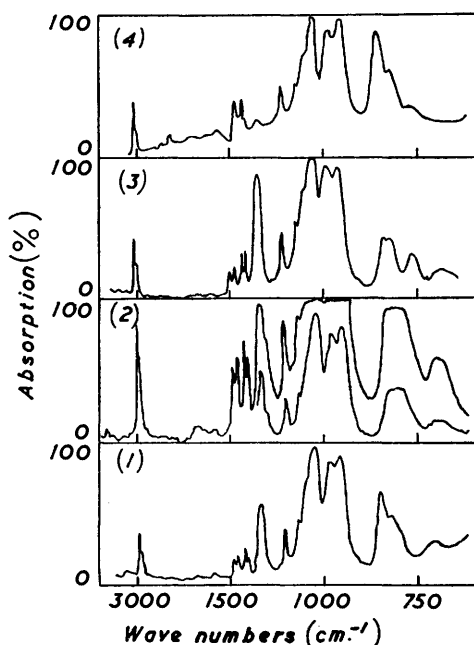
Since no results are available allocating a band position for absorption arising from a P-S-P linkage it has been necessary to find an alternative means of deciding to what extent this group may be present in any molecule. All of the compounds examined exhibit a band due to the P=S group but since it is broad and frequently overlaps others it is not a satisfactory basis for calculations. In compounds of type (1) the absorbance due to the P=O band should be approximately half that of compounds (2) and (3).



The relative change in intensity can be estimated as readily from $\int I_{\lambda} d\lambda$ [where I is $\log_{10}(T_0/T)$] as from $\int I_{\nu} d\nu$ since these are connected by constant factors for a given band.⁵ The spectrometer resolution was sufficiently great to satisfy Ramsay’s⁵ criterion such that the apparent integrated absorption coefficients should not differ from their true values by more than 5%. Use being made of this fact, the absorbance of the P=O stretching vibration (1300—1200 cm^{-1}) in the dialkylthiopyrophosphonates and the thio- and seleno-pyrophosphates has been compared with that in the fully oxygenated compound. Since the spectra were obtained from contact films it has been necessary to determine the relative absorbance of the P=O band by comparing its absorption with that of a band not appreciably affected by introduction of a sulphur atom; for this purpose the alkoxy-phosphorus

² Michalski and Wiczorkowski, *Roczniki Chem.*, 1954, **28**, 239.
³ Ford-Moore, Lermitt, and Stratford, *J.*, 1953, 1777.
⁴ A. and B. Arbusov, *J. prakt. Chem.*, 1931, **130**, 103.
⁵ Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72.

(EtO-P or PrⁱO-P) stretching vibration (*ca.* 1175 or 1110 cm.⁻¹, respectively) has been chosen and allocated an absorbance of unity. Thus, in a specimen of tetraethyl thiopyrophosphate, the relative values of $\int I_{\lambda} d\lambda$ at 1164 cm.⁻¹ (EtO-P) and 1261 cm.⁻¹ (P=O) are 27 and 81, respectively, giving a value for the relative absorbance of the P=O stretching vibration of 3. In the spectrum of tetraethyl pyrophosphate the corresponding figures are 33 and 220 giving a relative absorbance of 6.6; *i.e.* the degree of absorbance due to P=O in the sulphur-containing compound is $3/6.6 = 0.46$ of that of the oxygenated compound.



Infrared spectra of:
 (1) Tetraethyl thionopyrophosphate.
 (2) Tetraethyl selenonopyrophosphate.
 (3) Tetraethyl pyrophosphate.
 (4) Tetraethyl pyrophosphorothionate.

Table 1 gives the value of the relative absorbance of the P=O band determined as shown above and the degree of P=O absorption for the thio- and seleno-compounds prepared. The figures for (EtO)₂P(S)·O·P(S)(OEt)₂ are also given

TABLE 1. The relative absorbance (*A*) of the P=O band and the degree of P=O absorption (*B*) in compounds of the type R'R''P(X)·O·P(O)R'R''.

Compound			Spectrum	<i>A</i>	<i>B</i>	Compound			Spectrum	<i>A</i>	<i>B</i>
R'	R''	X	no.			R'	R''	X	no.		
EtO	EtO	S	1	3.0	0.46	EtO	Et	S	7	3.8	0.49
EtO	EtO	Se	2	3.2	0.48	EtO	Et	O	8	7.7	1.0
EtO	EtO	O	3	6.6	1.00	Pr ⁱ O	Me	S	9	3.1	0.53
(EtO) ₂ P(S)·O·P(S)(OEt) ₂			4	0.3	0.05	Pr ⁱ O	Me	O	10	5.8	1.00
EtO	Me	S	5	3.8	0.44	Pr ⁱ O	Et	S	11	2.7	0.50
EtO	Me	O	6	8.7	1.00	Pr ⁱ O	Et	O	12	5.4	1.00

The figures for the sulphur and selenium compounds are sufficiently close to 0.5 to show that the compounds exist almost exclusively in the thiono- (selenono-) structure and that the thio- (seleno-) form cannot be present to any marked extent.

EXPERIMENTAL

Alkyl Alkylphosphonochloridates.—Carbonyl chloride, dried by passage through sulphuric acid, was passed for 24 hr. into the dialkyl alkylphosphonate at <25°. After the mixture had been degassed at room temperature, the alkyl alkylphosphonochloridate was distilled at <50°. The following esters were thus obtained: ethyl methylphosphonochloridate, b. p. 37°/0.7 mm.,

n_D^{25} 1.4320; ethyl ethylphosphonochloridate, b. p. 43°/1 mm., n_D^{25} 1.4362; isopropyl methylphosphonochloridate, b. p. 40°/1 mm., n_D^{25} 1.4285; isopropyl ethylphosphonochloridate, b. p. 38°/1 mm., n_D^{25} 1.4322.

Tetraethyl Thionopyrophosphate.—This ester was prepared by the following modification of the method of Fiszer *et al.*¹ Diethyl phosphorochloridate (0.2 mole) was added dropwise with stirring and cooling to dry pyridine (0.3 mole) in benzene (100 ml.). Dry hydrogen sulphide was passed into the mixture for 4 hr. After the pyridinium chloride had been filtered off the benzene solution was evaporated under reduced pressure and finally warmed to 80°/0.1 mm., at which pressure the last traces of hydrochloride sublimed. Subsequent distillation afforded tetraethyl thionopyrophosphate (0.038 mole, 38%), b. p. 86—88°/5 × 10⁻⁴ mm., n_D^{20} 1.4505 (Fiszer *et al.* reported b. p. 120—122°/0.5 mm., n_D^{25} 1.4495).

A second specimen, prepared by Harman and Stiles's method,¹ was obtained in 68% yield, b. p. 81°/5 × 10⁻⁴ mm., n_D^{21} 1.4494, and had an infrared spectrum similar to that of the first.

Diethyl Dimethylthionopyrophosphonate.—Hydrogen sulphide was passed though a stirred solution of ethyl methylphosphonochloridate (33 g., 0.21 mole) and pyridine (26.8 g., 0.33 mole) in benzene at 10—15° for several hours. After filtration the product was worked up as described above. Fractional distillation of the crude product gave *diethyl dimethylthionopyrophosphonate* (10.5 g., 44%), b. p. 73—74°/3.5 × 10⁻⁴ mm., n_D^{20} 1.4679 (Found: C, 29.4; H, 6.75. C₈H₁₆O₄P₂S requires C, 29.3; H, 6.55%).

Diethyl Diethylthionopyrophosphonate.—Ethyl ethylphosphonochloridate (35 g., 0.22 mole) in pyridine and benzene was treated with hydrogen sulphide. Fractional distillation of the crude product gave *diethyl diethylthionopyrophosphonate* (23 g., 70%), b. p. 84°/10⁻³ mm., n_D^{25} 1.4652 (Found: C, 35.0; H, 7.7. C₈H₂₀O₄P₂S requires C, 35.0; H, 7.35%).

Diisopropyl Dimethylthionopyrophosphonate.—Similarly prepared, *diisopropyl dimethylthionopyrophosphonate* (9.5 g., 35%) had b. p. 74—75°/2 × 10⁻³ mm., n_D^{20} 1.4616 (Found: C, 35.0; H, 7.7. C₈H₂₀O₄P₂S requires C, 35.0; H, 7.3%).

Diisopropyl Diethylthionopyrophosphonate.—*Diisopropyl diethylthionopyrophosphonate* was obtained from isopropyl ethylphosphonochloridate (40 g., 0.24 mole) in 55% yield, b. p. 90°/7 × 10⁻⁴ mm., n_D^{20} 1.4516 (Found: C, 39.5; H, 7.95. C₁₀H₂₄O₄P₂S requires C, 39.7; H, 8.0%).

Tetraethyl Selenonopyrophosphate.—Tetraethyl selenonopyrophosphate was obtained in 55% yield (0.2 molar scale) by Michalski and Wiczorkowski's method;² it had b. p. 95°/6 × 10⁻⁴ mm., n_D^{25} 1.4582.

Tetraethyl Pyrophosphorothionate.—Commercial material was fractionally distilled to give a sample, b. p. 98°/4 × 10⁻⁴ mm., n_D^{20} 1.4761.

Dialkyl Dialkylpyrophosphonates.—The esters detailed in Table 2 were prepared on a 0.2 molar scale: water (0.1 mole) and pyridine (0.1 mole) were added dropwise to a stirred solution of alkyl alkylphosphonochloridate (0.2 mole) and pyridine (0.1 mole) in benzene at 0°. Stirring was continued for an hour after completion of the addition and the base hydrochloride then removed by filtration and sublimation as previously described; distillation then afforded the dialkyl dialkylpyrophosphonate.

TABLE 2. *Dialkyl dialkylpyrophosphonates* (RO)R'P(O)·O·P(O)(OR)R'.

R	R'	Yield, %	B. p./mm.	n (t°)	Formula	Analysis:			
						Found,		Calc.,	
					C	H	C	H	
Et	Me	85	68—70°/3.5 × 10 ⁻⁴	1.4360 (20)	C ₈ H ₁₆ O ₅ P ₂	31.5	6.9	31.3	7.0
Et	Et	60	70°/7 × 10 ⁻⁴	1.4302 (25)	C ₈ H ₂₀ O ₅ P ₂	37.3	7.9	37.2	7.75
Pr ⁱ	Me	51	78—80°/7 × 10 ⁻²	1.4270 (25)	C ₈ H ₂₀ O ₅ P ₂	37.5	8.0	37.2	7.75
Pr ⁱ	Et	55	65—66°/6 × 10 ⁻⁴	1.4304 (25)	C ₁₀ H ₂₄ O ₅ P ₂	41.8	8.4	41.95	8.45

Spectra.—Those presented in the Figure were obtained by using a Perkin-Elmer model 21 double-beam recording spectrophotometer.

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