Oxidation of Trivalent Phosphorus Compounds by Disulphides

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When methanol is used as solvent for the reaction between trivalent phosphorus compounds (Ph₂POMe, (MeO)₃P, and Ph₃P) and disulphides (RS•SR), oxidised phosphorus products which do not contain sulphur are obtained when the reaction proceeds by an ionic mechanism. It is suggested that these products are formed by methanolysis of the intermediate phosphonium ions [Ph₂(MeO)·PSR, (MeO)₃PSR, and Ph₃PSR]. The oxidation of triphenyl-phosphine by thiyl radicals is not affected by the use of alcohols as solvents.

The oxidation of trivalent phosphorus compounds by organic disulphides may occur by either an ionic¹ (Scheme 1) or a free radical² (Scheme 2) mechanism.



The reaction between triethyl phosphite and a number of disulphides has been shown to take place by an ionic mechanism. Triphenylphosphine has been found³ to react with diphenyl disulphide in the presence of water to give triphenylphosphine oxide, and it has been suggested that the reaction occurs by an ionic mechanism:

$$Ph_{3}P + PhS \cdot SPh \longrightarrow Ph_{3}^{\dagger} \cdot SPh \xrightarrow{H_{3}O} Ph_{3}^{\dagger} \cdot OH \longrightarrow Ph_{3}P \cdot OH$$

More recently Grayson and Farley⁴ have reported that secondary phosphines react with diphenyl disulphide in aqueous t-butyl alcohol to give phosphinothiolate esters (cyclo-C₆H₁₁)₂PH + 2PhS·SPh + H₂O \longrightarrow (cyclo-C₆H₁₁)₂P(:O)·SPh + 3PhSH.

It has now been found that the use of methanol as solvent for reactions between trivalent phosphorus compounds and disulphides, which occur by an ionic mechanism, leads to oxidised phosphorus compounds which do not contain sulphur. It is believed that these compounds are formed by methanolysis of the intermediate phosphonium ions (Scheme 3). When the

$$(MeO)_{3}^{+}SR \xrightarrow{\text{MeOH}} (MeO)_{4}PSR \xrightarrow{} (MeO)_{3}PO$$

$$\overline{SR} + RSH + RSMe$$

$$Scheme 3$$

oxidation takes place by a free-radical mechanism (Scheme 2) the use of alcohols as solvents does not alter the usual reaction path, *i.e.*, the radical intermediate (I) does not undergo alcoholysis.

¹ R. G. Harvey, H. I. Jacobson, and E. V. Jensen, J. Amer. Chem. Soc., 1963, **85**, 1618.

The reaction between methyl diphenylphosphinite and diphenyl disulphide in benzene was found to be exothermic. Although the products may have arisen by either an ionic or free-radical mechanism, it would seem unlikely that a radical mechanism would operate under such mild reaction conditions. Furthermore, the addition of hydroquinone had no effect upon the reac-Irradiation of a benzene solution of methyl tion. diphenylphosphinite containing dibenzyl disulphide, gave products typical of a free-radical reaction, e.g., bibenzyl. The reaction of methyl diphenylphosphinite with diphenyl disulphide and trimethyl phosphite with diphenyl and dibenzyl disulphides in methanolic solution, gave products consistent with an ionic mechanism. A methanolic solution of methyl diphenylphosphinite containing dibenzyl disulphide gave, on irradiation, products which indicated that both ionic and radical reactions had occurred.

$$\begin{array}{ccc} Ph_2 \stackrel{P}{ P} \cdot OMe & _ & \underbrace{\mathsf{MeOH}} \\ & & & \\ & & \\ S \cdot CH_2 Ph & \underbrace{\mathsf{S} \cdot CH_2 Ph} & \underbrace{\mathsf{MeOH}} \\ S \cdot CH_2 Ph & \\ PhCH_2 \cdot S^* + Ph_2 P \cdot OMe & \underbrace{\mathsf{Ph}_2 P(\mathsf{:}S) \cdot OMe + PhCH_2 \cdot S} \\ PhCH_2 \cdot S^* + PhCH_2 \cdot SH & \underbrace{\mathsf{Ph}_2 P(\mathsf{:}S) \cdot OMe + PhCH_2 \cdot S} \\ PhCH_2 \cdot + PhCH_2 \cdot SH & \underbrace{\mathsf{Ph}_2 P(\mathsf{:}S) \cdot OMe + PhCH_2 \cdot S} \\ \end{array}$$

The reaction between triphenylphosphine and diphenyl disulphide in methanol, was found to be exothermic. Under similar conditions dibenzyl disulphide did not react. The lower reactivity of dialkyl disulphides compared with diaryl disulphides towards trivalent phosphorus compounds is a well established fact.¹ The reaction between triphenylphosphine and dibenzyl disulphide in octan-2-ol gave products typical of a freeradical reaction. It has been previously mentioned that

$$PhCH_{2} \cdot S^{*} + Ph_{3}P \longrightarrow Ph_{3}P \cdot S + PhCH_{2}^{*}$$

$$PhCH_{2} \cdot S^{*} + C_{6}H_{13} \cdot CH(OH) \cdot CH_{3} \longrightarrow$$

$$PhCH_{2} \cdot SH + C_{6}H_{13} \cdot \dot{C}(OH) \cdot CH_{3}$$

$$C_{6}H_{13} \cdot \dot{C}(OH) \cdot CH_{3} + Radical \longrightarrow C_{6}H_{13} \cdot CO \cdot CH_{3}$$

$$PhCH_{2}^{*} + PhCH_{2} SH \longrightarrow PhCH_{3} + PhCH_{2}^{*}S$$

$$PhCH_{2}^{*} + PhCH_{2} \cdot S \cdot S \cdot CH_{2}Ph \longrightarrow (PhCH_{2})_{2}S + PhCH_{2} \cdot S^{*}$$

the methanol is believed to participate in ionic reactions by attacking the intermediate phosphonium ion (Scheme 3). A suggested mechanism for this reaction is shown in Scheme 4.

- ² C. Walling, O. H. Basedow, and E. S. Savas, J. Amer. Chem. Soc., 1960, **82**, 2181.
 - A. Schonberg and M. Z. Barakat, J. Chem. Soc., 1949, 892.
 M. Grayson and C. E. Farley, J. Org. Chem., 1967, 32, 236.



A similar mechanism has been previously proposed ⁵ for the reaction between trialkyl phosphites and carbon tetrachloride in alcoholic solution.

$$(R^{1}O)_{3}\overset{P}{\xrightarrow{}} CCl_{3} \longrightarrow (R^{1}O)_{3}\overset{\tilde{P}}{\xrightarrow{}} OR^{2} + CHCl_{3}$$

Control experiments showed that transesterification of the thiophosphorus esters does not occur under the reaction conditions, which supports the idea that the methanol participates by the route shown in Scheme 3.

It will have been noted that ionic reactions in methanolic solution with dibenzyl disulphide gave only sulphur-free oxidised phosphorus products whereas similar reactions with diphenyl disulphide did not. The reverse situation would be expected if the rate determining step of the reaction is the attack by the thioalkyl anion upon an alkoxy-group attached to the phosphorus atom since the toluene- α -thiyl anion is more reactive than the thienyl anion

This leads to the conclusion that the rate determining step occurs in the solvolytic displacement reaction (Scheme 4). If $k_1 \gg k_2$, *i.e.*, RSH is a good leaving group, methanol participation will be favoured. The experimental results indicate that toluene- α -thiol is a better leaving group than thiophenol. A similar observation, that ethanethiol is a better leaving group than thiophenol, was made ⁶ in a study of the acid catalysed hydrolysis of ethyl and phenyl 1-thio- β -D-glucopyranoside, a reaction which is thought to occur by an A-1 mechanism.

EXPERIMENTAL

All reactions were carried out under oxygen-free nitrogen. Methanol and octan-2-ol were distilled under nitrogen from calcium hydride prior to use.

Irradiation Conditions.—The light source, a 450w Hanovia medium pressure lamp was surrounded by a water cooled 'Pyrex' jacket. A 'Pyrex' tube $(1 \times 55 \text{ cm.})$, containing the mixture to be irradiated was rotated as near as possible to the jacket.

Spectra.---1H Nuclear magnetic resonance spectra were

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recorded for solutions in deuteriochloroform using a Varian A-60 spectrometer.

Gas-liquid Chromatography Analyses.—Toluene and methyl n-hexyl ketone were determined by means of a 2 m. Silicone gum rubber column at 70° and bibenzyl with the column at 180° . Thiophenol, methyl phenyl sulphide, and benzyl methyl sulphide were determined by means of a 2 m. Carbowax column at 135° and trimethyl phosphate with a 6 ft. Apiezon L column at 135° .

The Reaction of Methyl Diphenylphosphinite with Phenyl Disulphide in Benzene.—The disulphide (0.69 g.) was added to the phosphorus ester (1 g.) dissolved in benzene (10 ml.). The mixture was kept at 20° for 36 hr. Gas-liquid chromatographic analysis of the mixture showed that methyl phenyl sulphide (90% yield) had been produced. Evaporation of the benzene left an oil which on trituration with light petroleum (b. p. 40—60°) gave phenyl diphenylphosphinothiolate (0.86 g.), m. p. (from ether) 90—91° (Found: C, 69.8; H, 4.8; P. 10.3; S, 10.55. C₁₈H₁₈OPS requires C, 69.7; H, 4.9; P, 10.0; S, 10.3%).

The Reaction of Methyl Diphenylphosphinite with Benzyl Disulphide in Benzene.—A benzene solution (10 ml.) of the phosphorus ester (0.5 g.) containing dibenzyl disulphide (0.25 g.) was irradiated for 29 hr. Gas-liquid chromatographic analysis of the reaction mixture showed that bibenzyl had been produced in 40% yield. The solvent was removed by evaporation under reduced pressure to leave an oil which crystallised from methanol to give methyl diphenylphosphinothionate (0.14 g.), m. p. and mixed m. p. (from methanol) 84—86.5°. The mother-liquors were chromatographed on alumina (Spence type H). Elution with benzene gave methyl diphenylphosphinothionate (0.04 g.), m. p. and mixed m. p. (from methanol) 85—86°.

The Reaction of Methyl Diphenylphosphinite with Phenyl Disulphide in Methanol.-The disulphide (0.25 g.) was added to the phosphorus ester (0.5 g.) dissolved in methanol (2 ml.). Heat was evolved. Methanol (1 ml.) was added and the mixture kept at 20° for 4 hr. Gas-liquid chromatographic analysis showed that methyl phenyl sulphide (0.14 g.) and thiophenol (0.02 g.) had been produced. Evaporation of the solvent left an oil which was chromatographed on silica (10 g.). Elution with benzene gave methyl phenyl sulphide (0.09 g.) identified by i.r. spectroscopy and g.l.c. analysis. Elution with benzene-ether (17:3) gave phenyl diphenylphosphinothiolate (0.11 g.), m. p. and mixed m. p. (from ether) 89-90.5°. Elution with benzene-ether (4:1) gave methyl diphenylphosphinate (0.18 g.), m. p. and mixed m. p. (from light petroleum) $60-62^{\circ}.7$

The Reaction of Methyl Diphenylphosphinite with Benzyl Disulphide in Methanol.—The disulphide (0.25 g.) and the phosphorus ester (0.5 g.) were dissolved in methanol (10 ml.) and the mixture irradiated for 18 hr. Gas-liquid chromatographic analysis of the reaction mixture showed that benzyl methyl sulphide (0.13 g.) and toluene (0.09 g.) had been produced. Evaporation of the solvent left an oil which was chromatographed on silica (10 g.). Elution with benzene gave methyl diphenylphosphinothionate (0.22 g.), m. p. and mixed m. p. (from methanol) 84—86°. Elution with benzene-ether (3:1) gave methyl diphenyl-phosphinate, (0.14 g.), m. p. and mixed m. p. (from light petroleum) $60-62^{\circ}$.

⁷ R. S. Davidson, R. A. Sheldon, and S. Trippett, J. Chem. Soc. (C), 1966, 722.

 ⁵ A. J. Burn and J. I. G. Cadogan, J. Chem. Soc., 1963, 5788.
 ⁶ C. Bamford, B. Capon, and W. G. Overend, J. Chem. Soc., 1962, 5138.

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The Reaction of Trimethyl phosphite with Phenyl Disulphide in Methanol.—A mixture of the disulphide (8.8 g.) and the phosphorus ester (10 g.) was heated in methanol (40 ml.) at 65° for 2.5 hr. The solvent was distilled off at atmospheric pressure and the residual oil distilled under reduced pressure. Two fractions were obtained, b. p. 40—95° (7.17 g.) and 179—188° (5.78 g.) at 18 mm. The second fraction on redistillation gave phenyl dimethylphosphorothiolate (4.8 g.), b. p. 180—181° at 17 mm.; doublet at τ 6.34 ($J_{\rm PH}$ 12 c./sec.) (Found: C, 44.5; H, 5.2; P, 14.25; S, 14.6; C₈H₁₁O₃PS requires C, 44.0; H, 5.05; P, 14.2; S, 14.7%). The first fraction was dissolved in ether (15 ml.) and was washed with water (8 ml.). The aqueous phase was continuously extracted with ether to give trimethyl phosphate (1.04 g.), identified by g.l.c. and i.r. spectroscopy. The ethereal solution was washed

followed by ether extraction gave toluene- α -thiol (1 g.), identified as its 2,4-dinitrophenyl sulphide derivative, m. p. and mixed m. p. (from ethanol) 133-134°. The ether extract on evaporation gave benzyl methyl sulphide (3.8 g.), b. p. 195-196°, identified by g.l.c. and i.r. spectroscopy.

The Reaction of Triphenylphosphine with Phenyl Disulphide in Methanol.—The disulphide (1 g.) was added to triphenylphosphine (1·2 g.) dissolved in methanol (10 ml.). The mixture was kept at 65° for 3 hr. Gas-liquid chromatographic analysis of the reaction mixture showed that thiophenol (74% yield) and methyl phenyl sulphide (78% yield) had been produced. The methanol was removed by distillation. Crystallisation of the residue from benzene gave unchanged triphenylphosphine (0·24 g.). The motherliquors were diluted with ether (15 ml.) and the solution

The reaction of trivalent phosphorus compounds with disulphides

Phosphorus compounds	Solvent	Reaction conditions	Products from reaction with diphenyl disulphide $(\%)$		Products from reaction with dibenzyl disulphide $(\%)$	
Ph ₂ P·OMe	Benzene	20°, 36 hr.	Ph ₂ P(:O)·SPh PhSMe	(78) (90)		
Ph₂P•OMe	Benzene	<i>hv</i> , 16 hr.			$Ph_2P(:S) \cdot OMe$ $(PhCH_2)_2$	(31) a (40)
Ph ₂ P•OMe	Methanol	20°, 4 hr.	Ph ₂ P(:O)·SPh Ph ₂ P(:O)·OMe PhSMe PhSH	(30) (67) (100) (16)		
Ph₂P•OMe	Methanol	<i>hν</i> , 16 hr.			Ph ₂ P(:S)·OMe Ph ₂ P(:O)·OMe PhCH ₂ ·SMe PhMe	(43) (30) (93) (100)
$(MeO)_{3}P$	Methanol	65°, 2·5 hr.	(MeO) ₂ P(:O)•SPh (MeO) ₃ P:O PhSMe PhSH	(55) (19) (70) (8)	(MeO) ₃ P:O PhCH ₂ ·SMe PhCH ₂ ·SH	(48) (98) (38)
$Ph_{3}P$	Methanol	65°, 2·5 hr.	Ph₃P:O PhSMe PhSH	(70) (78) (74)	No reaction	
$\mathrm{Ph}_{3}\mathrm{P}$	Octan-2-ol	179°, 17 hr.			Ph3PS PhMe (PhCH2)2S C6H13COMe	(88) (50) (29)

^a Yield does not account for unchanged Ph₂P·OMe in reaction mixture.

with aqueous N-sodium hydroxide (10 ml.). Acidification of the aqueous washings, followed by ether extraction gave thiophenol, identified as its 2,4-dinitrophenylsulphide derivative (0.5 g.), m. p. and mixed m. p. (from ethanol) $122-123^{\circ}$. The ethereal solution gave on evaporation methyl phenyl sulphide (4 g.), b. p. $194-195^{\circ}$, identified by g.l.c. and i.r. spectroscopy.

The Reaction of Trimethyl Phosphite with Benzyl Disulphide in Methanol.—The disulphide (7 g.) was added to the phosphorus ester (7 g.) dissolved in methanol (32 ml.) and the mixture heated at 65° for $2 \cdot 5$ hr. The solvent was distilled off at atmospheric pressure and the residual oil distilled under reduced pressure. Most of the material (9.7 g.) distilled in the range $40-65^{\circ}$ at 0.5 mm. Very little residue remained. The distillate was dissolved in ether (25 ml.) and washed with water (8 ml.). Continuous ether extraction of the aqueous phase gave trimethyl phosphate (1.9 g.), identified by g.l.c. and i.r. spectroscopy. The ethereal solution was washed with aqueous N-sodium hydroxide (10 ml.). Acidification of the aqueous washings washed with aqueous N-sodium hydroxide (10 ml.) and water (10 ml.). Evaporation of the dried ethereal solution gave an oil which crystallised from ethanol to give triphenylphosphine oxide (0.9 g.), m. p. and mixed m. p. (from ethanol) 156-157°.

The Reaction of Triphenylphosphine with Benzyl Disulphide in Octan-2-ol.—The disulphide (4 g.) was added to the phosphine ($4\cdot5$ g.) dissolved in octan-2-ol (10 ml.). The mixture was heated under reflux for 17 hr. The cooled solution deposited triphenylphosphine sulphide ($4\cdot5$ g.), m. p. and mixed m. p. (from ethanol) 164—165°. Gas-liquid chromatographic analysis of solution showed that toluene ($0\cdot74$ g.) and methyl n-hexyl ketone ($0\cdot28$ g.) had been produced. The solvent was removed by distillation under reduced pressure. A residue was left which distilled at 105—110° at 1 mm. This material was chromatographed on alumina (100 g.). Elution with light petroleum gave an oil which crystallised at -15° from ethanol to give dibenzyl sulphide (1 g.), m. p. and mixed m. p. (from ethanol) $47--49^\circ$.

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Determination of the Stability of Phenyl Dimethylphosphorothiolate in Methanol.—The phosphorus ester (0.2 g.) in methanol (10 ml.), containing thiophenol (0.01 g.) was kept at 65° for 48 hr. Evaporation of the solvent left an oil the infrared and ¹H n.m.r. spectra of which were identical, with those of the starting material.

The Synthesis of Methyl Diphenylphosphinothionate.— Chlorodiphenylphosphine (1 g.) was added to sulphur (0.142 g.) dissolved in carbon disulphide (15 ml.). The mixture was heated under reflux for 3 hr. and then the solvent removed by distillation. The residual crude diphenylphosphinothioic chloride was added to sodium (0·104 g.) dissolved in methanol (10 ml.). The mixture was stirred at 20° for 15 hr. The precipitated sodium chloride was filtered off and then the *methyl diphenylphosphinothionate* crystallised out (0·8 g.), m. p. and mixed m. p. (from methanol) 87–88°, doublet at τ 6·36 ($J_{\rm PH}$ 14 c./sec.) (Found: C, 63·0; H, 5·35; P, 12·6; S,13·05; C₁₃H₁₃OPS requires C, 62·95; H, 5·25; P, 12·5; S, 12·9%).

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