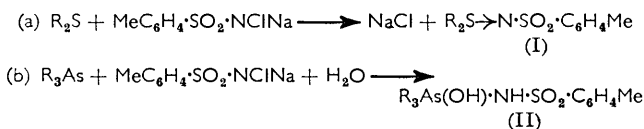


Constitution of the Adducts derived from Tertiary Phosphine Oxides and Arenesulphonamides

By David W. Allen, Department of Chemistry, Sheffield Polytechnic, Pond Street, Sheffield S1 1WB
 Frederick G. Mann,* University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW
 John C. Tebby, Department of Chemistry, North Staffordshire Polytechnic, College Road, Stoke-on-Trent ST4 2DE

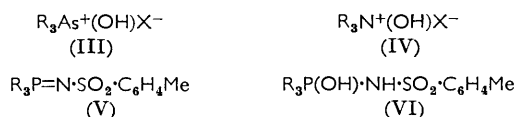
Evidence that tertiary phosphine oxides and arenesulphonamides combine in a 1:1 molecular ratio to form strongly hydrogen-bonded adducts, which do not dissociate in chloroform solution, is obtained from molecular weight, conductance, ^1H and ^{31}P n.m.r., and i.r. spectral measurements. Tertiary phosphines and anhydrous Chloramine-T give phosphine imides, which in the presence of water are hydrolysed to give the corresponding phosphine oxides and toluene-*p*-sulphonamide. Evidence is adduced supporting the six-membered, hydrogen-bonded, cyclic structure (VIII) for these adducts.

In early investigations on the nature and polarity of the co-ordinate link, Mann¹ noted the difference in type of product obtained when sodium *N*-chlorotoluene-*p*-sulphonamide (Chloramine-T) trihydrate reacted with (a) aliphatic sulphides, and (b) tertiary arsines (Scheme).



SCHEME

Reaction (a) proceeded rapidly and completely even when the liquid sulphide was shaken with a cold aqueous solution of Chloramine-T. The product (I) was first termed a sulphilimine, and later a sulphinimine: it can be designated as $R_2S=N\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$, one of the early examples of a sulphurane. Reaction (b) also proceeded readily with certain tertiary arsines, and the product (II) was apparently similar in type to compounds such as (III), which are readily formed by the union of a tertiary arsine oxide and an acid such as nitric or picric acid; aliphatic tertiary arsine oxides readily give similar derivatives (IV).



The reaction of tertiary phosphines in absolute ethanol with anhydrous Chloramine-T was later studied by Mann and Chaplin.² These phosphines (triphenylphosphine and various trialkylphosphines) usually gave phosphine imides (V); but the same reaction carried out in 98% ethanol gave products which were named 'hydroxy-sulphonamides' (VI), similar to the arsenic derivatives (II). The formation of these compounds was unexpected, for at that time the union of tertiary phosphine oxides with acids to give stable products was rare, and union with so weak an acid as toluene-*p*-sulphonamide appeared improbable. A detailed study was therefore made of the action of Chloramine-T, in anhydrous conditions and in rectified spirit, on trisubstituted triphenylphosphines; the *o*-, *p*-, and *m*- isomers of each phosphine were similarly

treated for comparison. The results are summarised in the Table,² and show that the position, rather than the

Interaction of trisubstituted triphenylphosphines, $\text{P}(\text{C}_6\text{H}_4\text{X})_3$, with Chloramine-T			
		(a) Anhydrous Chloramine-T in absolute ethanol	(b) Chloramine-T trihydrate in rectified spirit
<i>ortho</i> -	X		
	Me	Phosphine imide	Phosphine imide
	MeO	Phosphine imide	Phosphine imide + hydroxy-sulphonamide
<i>para</i> -	Cl	Phosphine imide	Phosphine imide
	Me	Phosphine imide	Phosphine imide + hydroxy-sulphonamide
	MeO Cl	Phosphine imide Phosphine imide	Hydroxy-sulphonamide Phosphine oxide + toluene-sulphonamide
<i>meta</i> -	Me	Syrup	Hydroxy-sulphonamide
	MeO	Glass	Hydroxy-sulphonamide
	Cl	Amorphous solid	Phosphine oxide + toluene-sulphonamide

nature, of the substituent determines the type of product.

The phosphine imide formulation (V) of the products obtained from the reactions in absolute ethanol has subsequently proved to be correct and recently the X-ray structure of triphenylphosphine *p*-tolylsulphonylimide (V; R = Ph) has been determined.³ However, comparable studies of the nature of the so-called hydroxy-sulphonamide (VI; R = Ph) do not appear to have been made. Formulation of these compounds as hydroxy-phosphoranes, involving a pentavalent phosphorus atom, appears improbable, especially in view of the fact that they can also be made by direct combination of a tertiary arylphosphine oxide and toluene-*p*-sulphonamide. Tertiary phosphine oxides are now known to be largely inert towards nucleophilic attack on phosphorus, except where the phosphorus atom is bound to strongly electron-withdrawing groups.⁴ Nucleophilic attack on phosphoryl phosphorus by toluene-*p*-sulphonamide to form, after subsequent protonation, a pentavalent hydroxyphosphorane (VI) appears unlikely.

Several of the 'hydroxy-sulphonamides' prepared in the original study have been re-examined. The properties of the 'hydroxy-sulphonamide' derived from tris-*p*-methoxyphenylphosphine and hydrated Chloramine-T in

⁴ A. J. Kirby and S. G. Warren, 'The Organic Chemistry of Phosphorus,' Elsevier, Amsterdam, 1967.

¹ F. G. Mann, *J. Chem. Soc.*, 1932, 958.

² F. G. Mann and E. J. Chaplin, *J. Chem. Soc.*, 1937, 527.

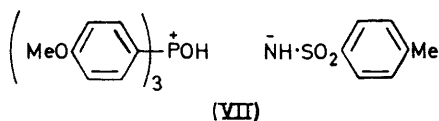
³ A. F. Cameron, N. J. Hair, and D. G. Morris, *Chem. Soc. Autumn Meeting, York, 1971; Chem. Comm.*, 1971, 918.

ethanol are typical of the hydroxy-sulphonamides and will now be discussed.

Direct union of equimolar proportions of tris-*p*-methoxyphenylphosphine oxide and toluene-*p*-sulphonamide in toluene, gave an adduct identical with that prepared *via* the phosphine and hydrated Chloramine-T in ethanol. Molecular weight determinations showed that the adduct was not dissociated to any significant extent in chloroform solution.

³¹P N.m.r. studies of the adduct rule out a pentacovalent hydroxyphosphorane structure. The ³¹P spectrum of the adduct in chloroform solution exhibited a signal at $\delta -30$ p.p.m. (relative to 85% H₃PO₄); the spectrum of the corresponding phosphine oxide exhibited a signal at $\delta -29.5$ p.p.m., indicating that the shielding of the phosphorus in the adduct is similar to that in the phosphine oxide, and different from the large positive chemical shifts generally observed for pentaco-ordinate phosphoranes.

Alternative formulations for the adduct such as the hydroxyphosphonium salt (VII), which could be considered as being produced by dissociation of a pentaco-ordinate hydroxyphosphorane, were ruled out by the results of conductance studies. A solution of the adduct (0.002M in chloroform) had a very low conductivity compared with a similar solution of methyltriphenylphosphonium iodide. In addition, the absence of the cation of (VII) was indicated when a deuteriochloroform solution



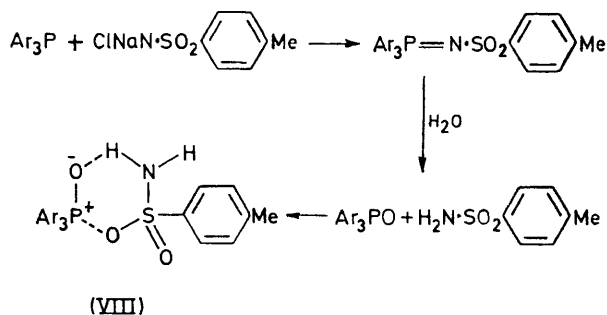
of tris-*p*-methoxyphenylphosphine oxide, when treated with sulphuric acid, failed to produce any shift in the ¹H n.m.r. signal due to the methoxy-groups.

In view of the ease of formation of the adduct from the phosphine oxide and toluene-*p*-sulphonamide in toluene solution, a hydrogen-bonded structure is most easily envisaged. Recently, hydrogen-bonded adducts of triphenylphosphine oxide with *N*-methyltoluene-*p*-sulphonamide have been described,⁵ and similar hydrogen-bonded adducts of phosphine oxides with phenols,⁶ and also with strong mineral acids,⁷ have been reported. The i.r. spectra of our adducts are in keeping with such a hydrogen-bonded structure; for example, the spectrum of the adduct (VIII; Ar = *p*-tolyl) shows $\nu_{P=O}$ 1165, whereas that of the corresponding phosphine oxide, (*p*-tolyl)₃PO, shows $\nu_{P=O}$ 1190 cm⁻¹. The N-H stretching absorption in the free sulphonamide appears as a doublet at 3240 and 3330 cm⁻¹, whereas in the foregoing adduct, it occurs as a broad band centred at 3260 cm⁻¹.

These findings support a N-H...O⁻-P⁺ hydrogen bond. The i.r. bands due to the sulphonyl group show marked

sharpening in the adducts. Together with the molecular weight measurements, this indicates that the adducts may also contain a P⁺...O⁻-S⁺ electrostatic interaction which would be present in an internally hydrogen-bonded structure such as (VIII). Similar interactions have been observed in sulphonate phosphonium betaines,⁸ and in our adducts they would reinforce the hydrogen-bonding and explain the remarkable stability of these adducts to dissociation. A hydrogen-bonded structure is also in keeping with the ¹H and ³¹P n.m.r. data on the adducts.

The cumulative physical evidence thus strongly indicates that these adducts have the six-membered hydrogen-bonded ring system (VIII).



The reaction of tertiary phosphines with Chloramine-T is now interpreted in the following way (see Scheme): in absolute ethanol the weakly basic phosphine imide is obtained but in the presence of water this is rapidly hydrolysed to the phosphine oxide and toluene-*p*-sulphonamide, which then unite to give the adduct (VIII). The results summarised in the Table show that the susceptibility of the phosphine imide to hydrolysis is least when *ortho*-substituents hinder the approach of water to the P-N bond. On the other hand the stability of the adduct of the phosphine oxide and toluene-*p*-sulphonamide is least when the *P*-phenyl ring bears the electron-withdrawing chlorine atom. This latter observation suggests that the chlorine atom increases the electron-deficiency of the phosphorus atom, which then demands increased donation of electrons from the oxygen atom, presumably mainly by *p*_π-*d*_π bonding. This leads to a weaker hydrogen bond and possibly a weaker attraction between the phosphorus atom and sulphonate groups.

For comparison with the foregoing phosphorus compounds, it may be noted that tris-(2-chlorovinyl)arsine reacts with hydrated Chloramine-T to give an adduct of type (II);⁹ triphenyl-, tri-*o*-tolyl-, and tri-*p*-tolylarsines react under strictly anhydrous conditions to give arsine imides, R₃As:N·SO₂·C₆H₄Me-*p*; ² dimethylphenylarsine and methylphenethylphenylarsine react to give the corresponding tertiary arsine oxides.¹

⁵ D. Hadzi, *J. Chem. Soc.*, 1962, 5128.

⁸ M. A. Shaw, J. C. Tebby, R. S. Ward, and D. H. Williams, *J. Chem. Soc. (C)*, 1968, 2795.

⁹ F. G. Mann and W. J. Pope, *Trans. Chem. Soc.*, 1922, 121, 1754.

⁶ V. A. Shokol, L. I. Maliakov, and G. J. Derkach, *Zhur. obshchei Khim.*, 1966, 36, 930 (*Chem. Abs.*, 1966, 65, 12,229).

⁷ M. Schindlbauer and H. Stenzenberger, *Monatsh.*, 1968, 99, 2468.

EXPERIMENTAL

^1H N.m.r. spectra were recorded at 60 MHz on a Perkin-Elmer R10 spectrometer with tetramethylsilane as internal standard. ^{31}P N.m.r. spectra were recorded at 24 MHz on the same instrument, with 85% phosphoric acid as external standard. I.r. spectra were recorded with a Perkin-Elmer 350 spectrophotometer. Except where otherwise stated, the phosphine oxides and their adducts with toluene-*p*-sulphonamide were prepared as described by Mann and Chaplin.² Conductance measurements were carried out in chloroform solution, by use of a Lock conductance bridge.

*The Adduct (VIII; Ar = *p*-MeO·C₆H₄).*—Tris-*p*-methoxyphenylphosphine oxide (0.368 g, 1 mmol) and toluene-*p*-sulphonamide (0.171 g, 1 mmol) were heated in toluene (10 ml). When cooled the solution deposited diamond-shaped crystals, m.p. 122—123°, identical with the product isolated from the reaction of tris-*p*-methoxyphenylphosphine and hydrated Chloramine-T in rectified spirit (lit.,² m.p. 121°, ν_{max} (mull) 3260br cm⁻¹ (NH), P=O region complex, τ (CDCl₃) 2.1—3.25 (16H, m), 4.48 (2H, m), 6.22 (9H, s), 7.65 (3H, s), δ ^{31}P (CHCl₃) —30 p.p.m. [Found: C, 62.6; H, 5.6; N, 2.4%; *M* (by ebulliometry in chloroform), 493. C₂₈H₃₀NO₆PS requires C, 62.3; H, 5.6; N, 2.6%; *M*, 539]. A 0.002M-solution of the adduct in chloroform had negligible electrical conductivity.

*Tris-*p*-methoxyphenylphosphine Oxide.*—The oxide, m.p. 142—143°, had δ ^{31}P (CHCl₃) —29.5 p.p.m., τ (CDCl₃) 2.2—3.2 (12H, m) and 6.22 (9H, s) (the spectrum was unaffected by the dropwise addition of sulphuric acid).

*The Adduct (VIII; Ar = *o*-MeO·C₆H₄).*—The adduct,

derived from tris-*o*-methoxyphenylphosphine and hydrated Chloramine-T, had m.p. 151—152° (lit.,² 149°), ν_{max} (KBr) 2940, 3395 (NH), and 1168 cm⁻¹ (P=O), δ ^{31}P (CHCl₃) —27 p.p.m.

*Tris-*o*-methoxyphenylphosphine Oxide.*—The adduct (VIII; Ar = *o*-MeO·C₆H₄) was triturated with aqueous 2*N*-sodium hydroxide, and the liberated phosphine oxide was collected and washed with water; to ensure completion of the reaction the oxide was moistened with ethanol and the trituration repeated. The white oxide, when dried *in vacuo* at 80°, had m.p. 217—218° (lit.,¹⁰ m.p. 215—217°), δ ^{31}P (CHCl₃) —26.5 p.p.m., τ (CDCl₃) 2.25—2.70 (6H, m, ArH), 2.90—3.20 (6H, m, ArH), 6.48 (9H, s, MeO).

*The Adduct (VIII; Ar = *m*-MeO·C₆H₄).*—The adduct derived from tris-*m*-methoxyphenylphosphine oxide had m.p. 114—115° (lit.,² 112°), ν_{max} (KBr) 3020, 3160, and 3310 (NH), and 1165 and 1190 cm⁻¹ (P=O, S=O), δ ^{31}P (CHCl₃) —31 p.p.m.

*Tris-*m*-methoxyphenylphosphine Oxide.*—The oxide, m.p. 154—155° (lit.,² 151—152°) had δ ^{31}P (CHCl₃) —30.5 p.p.m.

*The Adduct (VIII; Ar = *p*-MeC₆H₄).*—The adduct derived from tri-*p*-tolylphosphine oxide had m.p. 108° (lit.,² 106°), ν_{max} (KBr, mull, or chloroform) 3260br (NH) and 1165 cm⁻¹ (P=O), τ (CDCl₃) 2.2—2.95 (16H, m) and 7.64 (12H, s), δ ^{31}P (CHCl₃) —30.5 p.p.m.

*Tri-*p*-tolylphosphine Oxide.*—The oxide had δ ^{31}P (CHCl₃) —30 p.p.m. and $\nu_{\text{P=O}}$ 1190 cm⁻¹.

[2/995 Received, 4th May, 1972]

¹⁰ G. Wittig, H. D. Weigmann, and M. Schlosser, *Chem. Ber.*, 1961, **94**, 676.