118. *The Polarity of the Co-ordinate Link. Part II. The Influence of Aromatic Substitution on the Stability of the Phosphinimines.*

By Frederick G. Mann and E. James Chaplin.

In Part I (Mann, J., 1932, 958) it was shown that there is a marked difference in the type of product obtained by the action of sodio-*N*-chloro-*p*-toluenesulphonamide ("chloramine-T"), $CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}NNaCl,3H_2O$, on organic sulphides and on tertiary arsines. Sulphides react readily (often in cold aqueous suspension) with chloramine-T to give sulphilimines (I), whereas tertiary arsines give the corresponding hydroxy-sulphonamides (II). This difference was attributed to the fact that the co-ordinate link joining the

$$R_2S + NNaCl{\cdot}SO_2{\cdot}C_7H_7 = NaCl + R_2S{\rightarrow}N{\cdot}SO_2{\cdot}C_7H_7 \quad \text{(I.)}$$

$$R_3As + NNaCl{\cdot}SO_2{\cdot}C_7H_7 + H_2O = NaCl + AsR_3(OH){\cdot}NH{\cdot}SO_2{\cdot}C_7H_7 \quad \text{(II.)}$$

sulphur and the nitrogen atom in the sulphilimines is apparently devoid of polar properties, and such compounds are therefore stable even in the presence of water. The co-ordinate link joining the arsenic and the nitrogen atom in the arsinimines, $R_3As{\rightarrow}N{\cdot}SO_2{\cdot}C_7H_7$ (which are presumably the initial product in the above reaction) has, however, such strongly polar properties that the compound immediately combines with water to form the hydroxy-sulphonamide (II). This behaviour is parallel to that shown by most tertiary arsine oxides, $R_3As{\rightarrow}O$, where the co-ordinate link is so strongly polar that combination occurs freely, not only with acids such as nitric acid to give hydroxy-nitrates,

$AsR_3(OH)NO_3$ (a class of compound precisely similar to the hydroxy-sulphonamides), but also with water to give compounds such as $AsR_3(OH)_2$ and $AsR_3(OH)\cdot O\cdot AsR_3(OH)$. The tertiary arsine hydroxy-sulphonamides were prepared also by the direct union of the corresponding arsine oxides and *p*-toluenesulphonamide, their constitution thus being proved.

The action of chloramine-T on tertiary phosphines has now been investigated, each phosphine, however, having been treated (*a*) with the anhydrous reagent in absolute-alcoholic solution, and (*b*) with the hydrated reagent in rectified spirit. It is clear, therefore, that under conditions (*a*) only a true phosphinimine, $R_3P\rightarrow N\cdot SO_2\cdot C_7H_7$, could be formed, whereas under (*b*) a phosphinimine or the hydroxyphosphine-sulphonamide (III), could be formed according to the strength of the polarity of the co-ordinate link in the initial phosphinimine.

(III.) $PR_3(OH)\cdot NH\cdot SO_2\cdot C_7H_7$ $(C_7H_7\cdot SO_2\cdot NH\cdot PPh_3)_2N\cdot SO_2\cdot C_7H_7$ (IV.)

Triphenylphosphine under conditions (*a*) was found to give the true *phosphinimine*, $Ph_3P\rightarrow N\cdot SO_2\cdot C_7H_7$, whereas under (*b*) it gave NN-*bis*-(p-*toluenesulphonamidotriphenylphosphine*)-p-*toluenesulphonamide* (IV). The latter compound is identical in type with that given by triphenylarsine (Mann, *loc. cit.*), and it is noteworthy that no other phosphines or arsines were found to give this complex type of sulphonamide instead of the simple hydroxy-sulphonamide such as (III).

The effect of aromatic substituents in the triphenylphosphine molecule was then investigated, and the reaction of the *o*-, *m*-, and *p*-forms of tritolylphosphine, trianisylphosphine, $P(CH_3O\cdot C_6H_4)_3$, and trischlorophenylphosphine, $P(C_6H_4Cl)_3$, with chloramine-T under conditions (*a*) and (*b*) determined. The results are summarised in the table.

The Interaction of Tri-substituted Triphenylphosphines, $P(C_6H_4X)_3$, *with Chloramine-T.*

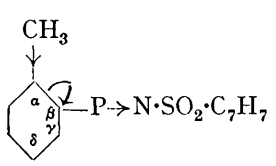
	Substituent, X.	(*a*) Anhydrous chloramine-T in absolute alcohol.	(*b*) Hydrated chloramine-T in rectified spirit.
Ortho-.	CH_3–	Phosphinimine	Phosphinimine
	CH_3O–	Phosphinimine	Phosphinimine + hydroxy-sulphonamide
	Cl–	Phosphinimine	Phosphinimine
Para-.	CH_3–	Phosphinimine	Phosphinimine + hydroxy-sulphonamide
	CH_3O–	Phosphinimine	Hydroxy-sulphonamide
	Cl–	Phosphinimine	Phosphine oxide + toluenesulphonamide
Meta-.	CH_3–	Syrup	Hydroxy-sulphonamide
	CH_3O–	Glass	Hydroxy-sulphonamide
	Cl–	Amorphous solid	Phosphine oxide + toluenesulphonamide

Tri-o-*tolylphosphine* thus gives a *phosphinimine* under both conditions (*a*) and (*b*), the presence of the three *o*-methyl groups suppressing the polarity of the P→N link and so inhibiting the formation of a hydroxy-sulphonamide; the same effect was found in the corresponding phosphine oxide, $(o\text{-}CH_3\cdot C_6H_4)_3P\rightarrow O$, in which the P→O link is too feebly polar to allow combination with *p*-toluenesulphonamide to give a hydroxy-sulphonamide. A similar but weaker effect was found with tri-*p*-tolylphosphine, which under conditions (*b*) gave a mixture of the *phosphinimine* and the *hydroxy-sulphonamide* : the polarity of the P→N link is evidently being less strongly suppressed by the three *p*-methyl groups, thus permitting some hydroxy-sulphonamide to be formed in the presence of water. Moreover, *p*-tolylphosphine oxide combined with *p*-toluenesulphonamide, but the hydroxy-sulphonamide so obtained dissociated again into its components in certain organic solvents. *Tri*-m-*tolylphosphine* under the anhydrous conditions (*a*) gave, however, only a thick viscous syrup. All attempts to isolate a crystalline derivative—either by the use of solvents, or by keeping the syrup under various conditions for many months—failed completely, and it is clear that a well-defined phosphinimine cannot be obtained. A very stable *hydroxy-sulphonamide* was, however, readily obtained when the *m*-tolylphosphine was treated with chloroamine-T under conditions (*b*), and also when the *phosphine oxide* was treated with *p*-toluenesulphonamide.

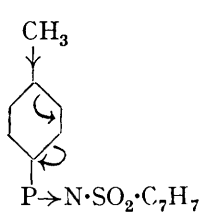
The effect of the methoxy-group in the trianisylphosphines, although similar through-

out to that of the methyl group in the tolylphosphines, was weaker, in that under conditions (*b*) the o-*methoxy-phosphine* gave a mixture of *phosphinimine* and *hydroxy-sulphonamide*, and the p-*methoxy-phosphine* gave solely the *hydroxy-sulphonamide*. The tris-chlorophenylphosphines also gave similar results with one marked exception, *viz.*, that the p- and the m-*chloro-phosphine* under conditions (*b*) did not give the expected hydroxy-sulphonamides but a mixture of the *phosphine oxide* and *p*-toluenesulphonamide.

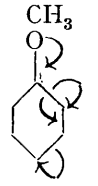
A complete theoretical interpretation of the above results is difficult. They are, however, clearly dependent on the fact that the three substituent groups studied (CH_3, CH_3O, and Cl) are all *op*-directing. Such groups cause an electron drift from themselves towards the benzene ring, either by the inductive effect of the substituent group followed by the resulting electromeric effect (V*a* and V*b*) or by the electromeric effect alone (VI and VII) : in either case, an increase in the electrons on the β- and the δ-carbon atoms results. In the *o*-compounds, the cumulative effect of this electron pressure on the β-



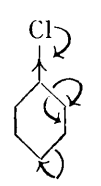
(V*a*.)



(V*b*.)



(VI.)



(VII.)

carbon atoms of the three phenyl groups must be to decrease the dipole of the P→N group to which these atoms are directly attached (as in V*a*) and so to diminish the polarity of this group. In the *p*-compounds, the electron pressure on the δ-carbon atoms has the same result, but the effect is weaker owing to the greater distance involved (V*b*). The γ-carbon atoms are, however, almost unaffected by this electron drift, and hence in the *m*-compounds the P→N group exerts its full polarity : this is so great that apparently no well-defined phosphinimine exists, but a very stable hydroxy-sulphonamide is readily formed. In the chlorophenyl compounds (VII) the electromeric effect initiated by the chlorine atoms is, however, opposed by the inductive effect of these atoms, and this weakening may explain why in this series the phosphine oxides were obtained in place of the expected hydroxy-sulphonamides. On the other hand, contrary to the experimental results, the electromeric effect of the methoxy-group (VI) should have proved stronger than the inductive effect of the methyl group (V*a* and V*b*). The results are clearly unaffected by the *p*-toluenesulphonyl group, in view of the reaction of chloramine-T with sulphides and arsines under conditions (*b*).

This interpretation of the effect of the three *op*-directing groups would be strongly confirmed by similar experiments with derivatives of triphenylphosphine having *m*-directing substituent groups, for the above results should be reversed throughout, and only the *m*-substituted phosphine should readily give a stable phosphinimine. The Grignard reaction cannot be used for the preparation of such phosphines, however, and other synthetic methods have hitherto proved unsuccessful. Nevertheless, it is noteworthy that tri-*m*-nitrophenylphosphine oxide (Challenger and Wilkinson, J., 1924, **125**, 2675) will not combine with *p*-toluenesulphonamide : this is in accord with the above interpretation, since the *m*-nitro-groups should suppress the polar properties of the co-ordinate link in the phosphine oxide.

In view of the above results, the three tritolylarsines have now been treated with anhydrous chloramine-T under conditions (*a*), and precisely similar results obtained, the *o*- and *p*-tolylarsines giving true *arsinimines*, $(CH_3{\cdot}C_6H_4)_3As{\rightarrow}N{\cdot}SO_2{\cdot}C_7H_7$, whereas no well-defined product could be obtained from *m*-tolylarsine. The fact that all three tolylarsines give hydroxy-sulphonamides under conditions (*b*) (Mann, *loc. cit.*), whereas only the *p*- and the *m*-tolylphosphine do so, is evidently due to the As→N group having a greater polarity than the P→N group : this increase in polarity as the positive atom is

replaced by a heavier atom in the same periodic group is to be expected on other grounds (Sidgwick, "The Covalent Link in Chemistry" **1933**, p. 153).

The lower trialkylphosphines readily give phosphinimines under conditions (*a*); hydroxy-sulphonamides are apparently formed under conditions (*b*), but their low melting points and high solubility in most solvents make their isolation and purification difficult.

Since the phosphinimines are stereochemically analogous to the phosphine oxides (Meisenheimer and co-workers, *Ber.*, **1911**, **44**, 356; *Annalen*, **1926**, **449**, 213), attempts are now being made to prepare a suitable dissymmetric phosphinimine for optical resolution purposes.

Experimental.

The description of the preparation of each phosphine is followed by an account of its behaviour when under conditions (*a*) and (*b*) (see p. 528). The anhydrous chloramine-T was prepared by exposing the hydrated material to phosphoric oxide in a vacuum until the theoretical loss in weight was obtained. All derivatives, unless otherwise stated, were isolated as colourless crystals.

Triphenylphosphine was prepared by Dodonov and Medox's method (*Ber.*, 1928, **61**, 910). (*a*) Solutions of the phosphine (3 g.) and anhydrous chloramine-T (2·6 g., 1 mol.), each in hot absolute alcohol (40 c.c.), were mixed, sodium chloride rapidly separating. The mixture was boiled for 1 hour under reflux in a dry apparatus closed with a calcium chloride tube. The solution was then filtered, concentrated by direct distillation, and finally taken to dryness in a vacuum desiccator, crystals rapidly separating meanwhile. The complete dry residue, thrice recrystallised from benzene, gave *triphenylphosphine*-p-*toluenesulphonylimine*, m. p. 187° (Found: C, 70·2; H, 5·1; N, 3·2; S, 7·2. $C_{25}H_{22}O_2NSP$ requires C, 69·6; H, 5·1; N, 3·2; S, 7·4%). Consistent values for carbon were very difficult to obtain with all derivatives of triphenylphosphine, which thus differed from other phosphines studied, but resembled triphenylarsine (cf. Mann, *loc. cit.*; Davies, Pearse, and Jones, J., 1929, 1263). (*b*) A similar experiment, in which solutions of the phosphine (4 g.) and hydrated chloramine-T (4·4 g., 1 mol.) each in hot rectified spirit (50 c.c.) were used, gave on evaporation a syrup which rapidly solidified. Recrystallisation from benzene gave NN-*bis*-(p-*toluenesulphonamidotriphenylphosphine*)-p-*toluenesulphonamide* (IV), m. p. 138° (Found: H, 5·3; N, 4·1; S, 9·1; P, 5·7. $C_{57}H_{53}O_6N_3S_3P_2$ requires H, 5·2; N, 4·1; S, 9·3; P, 6·0%). The m. p.'s of this compound and of *p*-toluenesulphonamide are identical: that of a mixture is very much lower.

Triphenylphosphine oxide, m. p. 154° (Michaelis, *Annalen*, 1885, **229**, 305), was obtained by the addition of 1 mol. of bromine to the phosphine, followed by hydrolysis with hot sodium hydroxide solution; when benzene solutions of the oxide and of *p*-toluenesulphonamide (1·0 or 1·5 mols.) were boiled under reflux for 30 minutes and cooled, the above tris-sulphonamide was again obtained.

Tri-o-*tolylphosphine* was obtained by addition of a solution of phosphorus trichloride (6 g.) in ether (40 c.c.) to a Grignard reagent prepared by the action of magnesium (5·2 g.) upon *o*-bromotoluene (37 g.) dissolved in ether (100 c.c.); hydrogen was bubbled continuously through the well-stirred mixture during the addition. The final solution was then chilled, and the product hydrolysed with dilute hydrochloric acid. The ethereal layer was separated, dried over sodium sulphate, and the ether removed by distillation. The product was then heated to 280—290° under reduced pressure in a hydrogen atmosphere to remove by-products, and the residue when cold was crystallised from alcohol to give the phosphine, m. p. 125° (Found: C, 82·8; H, 7·1. $C_{21}H_{21}P$ requires C, 82·9; H, 7·0%).

(*a*) Solutions of the phosphine (10 g.) and anhydrous chloramine-T (7·5 g.), each in hot absolute alcohol (200 c.c.), were mixed and boiled under reflux for 2 hours. The solution was filtered, concentrated by distillation, and finally taken to dryness in a desiccator; recrystallisation of the solid from absolute alcohol gave *tri*-o-*tolylphosphine*-p-*toluenesulphonylimine*, m. p. 188° (Found: C, 71·1; H, 6·0; N, 3·0. $C_{28}H_{28}O_2NSP$ requires C, 71·0; H, 6·0; N, 3·0%). No other product could be isolated from the mother-liquors from the recrystallisation.

(*b*) A similar experiment, with 1 mol. of hydrated chloramine-T in rectified spirit, again gave the phosphinimine. The alcoholic mother-liquor from the first recrystallisation of the crude product was evaporated to dryness, and the residue, after recrystallisation from ethyl carbonate and then from alcohol, gave *tri*-o-*tolylphosphine oxide*, $P(C_7H_7)_3O,\frac{1}{2}H_2O$, m. p. 153° (Found: C, 76·7; H, 6·8. $C_{42}H_{44}O_3P_2$ requires C, 76·6; H, 6·7%), identical with that obtained by adding bromine to the phosphine and then boiling with aqueous sodium hydroxide for 12 hours to complete the hydrolysis. Since *p*-toluenesulphonamide was also isolated from

the mother-liquor, it is clear that the formation of the phosphinimine in rectified spirit is accompanied by that of some phosphine oxide and toluenesulphonamide, but that these do not combine to form a stable hydroxy-sulphonamide. This fact was confirmed by boiling an alcoholic solution of the oxide and the sulphonamide (1 mol.) for 30 minutes; evaporation of the solvent gave a solid residue from which the unchanged components were recovered by crystallisation.

Tri-*p*-tolylphosphine, m. p. 146°, was prepared as for the *o*-isomeride; Michaelis (*Annalen*, 1901, **315**, 79) prepared it by the action of sodium on a mixture of phosphorus trichloride and *p*-bromotoluene in ether.

(*a*) The phosphine was treated with anhydrous chloramine-T as described for the *o*-compound. Recrystallisation of the solid residue from alcohol gave *tri*-p-*tolylphosphine*-p-*toluenesulphonylimine*, m. p. 174° (Found: C, 71·1; H, 6·0; N, 2·9%).

(*b*) Reaction under these conditions, followed by evaporation, afforded a solid, which, recrystallised from alcohol, furnished the above phosphinimine. The alcoholic mother-liquor was evaporated to dryness, and the residue, recrystallised from ethyl carbonate, gave *hydroxy-tri*-p-*tolylphosphine*-p-*toluenesulphonamide*, m. p. 106° (Found: C, 68·4; H, 6·1; N, 2·8. $C_{28}H_{30}O_3NSP$ requires C, 68·4; H, 6·15; N, 2·85%). The same product was obtained by dissolving equimolecular quantities of the phosphine oxide, $P(C_7H_7)_3O,\frac{1}{2}H_2O$ (Michaelis, *loc. cit.*), and of *p*-toluenesulphonamide in hot alcohol, evaporating the solution to dryness, and recrystallising the residue from ethyl carbonate. The hydroxy-sulphonamide is unstable in solution, since a hot benzene solution of the pure compound on cooling deposited free *p*-toluenesulphonamide; no evidence that it would undergo dehydration to the phosphinimine could be obtained, however, a sample being unchanged after 8 months' exposure to phosphoric oxide in a vacuum.

Tri-m-*tolylphosphine*, prepared as for the *o*-isomeride, and recrystallised from alcohol, had m. p. 100° (Found: C, 82·6; H, 6·8%).

(*a*) The phosphine was treated with anhydrous chloramine-T as before, and evaporation of the solution gave a thick viscous syrup, which did not solidify when kept in a desiccator for a year; all attempts at recrystallisation from numerous solvents proved unsuccessful, the substance either remaining in solution or separating again as an intractable syrup. On one occasion a sample of the syrup was repeatedly washed with petrol (b. p. 60—80°) in which it was almost insoluble, and was then exposed to the air for 3 days, solidification slowly occurring; the product could be recrystallised only from ethyl carbonate, which deposited *hydroxytri*-m-*tolylphosphine*-p-*toluenesulphonamide*, m. p. 98° (Found: C, 68·3; H, 6·1; N, 3·0%).

(*b*) The product obtained under these conditions solidified immediately the alcohol was evaporated. Recrystallisation from either ethyl carbonate or alcohol readily furnished the hydroxy-sulphonamide (Found: C, 68·4; H, 6·2%), the m. p. being unchanged on admixture with the sample obtained as in (*a*); no other product could be detected.

Tri-m-*tolylphosphine oxide*, prepared by the addition of bromine to the phosphine, followed by hydrolysis and final recrystallisation from petrol (b. p. 100—120°), had m. p. 111° (Found: C, 78·7; H, 6·6. $C_{21}H_{21}OP$ requires C, 78·75; H, 6·6%). It is noteworthy that the phosphine dibromide was completely hydrolysed by 2 hours' boiling with aqueous sodium hydroxide solution, in contrast to the 12 hours required for the *o*-compound. Equimolecular quantities of the oxide and of *p*-toluenesulphonamide in hot alcoholic solution rapidly combined to give the above hydroxy-sulphonamide.

Tri-o-*anisylphosphine*.—*o*-Bromoanisole, prepared by the method of Diels and Bunzl (*Ber.*, 1905, **38**, 1496), was converted into a Grignard reagent and then treated with phosphorus trichloride, the same proportions of reagents and solvent being used as in the preparation of triphenylphosphine. The final chilled solution was now, however, hydrolysed with excess of an aqueous solution of ammonium chloride. The *phosphine*, being almost insoluble in cold ether, separated out during the hydrolysis, and was collected, dried, and recrystallised from much alcohol; it had m. p. 204° (Found: C, 71·4; H, 6·1. $C_{21}H_{21}O_3P$ requires C, 71·6; H, 6·0%).

(*a*) Solutions of the phosphine (3·0 g.) and anhydrous chloramine-T (2·0 g.) in hot absolute alcohol (200 and 50 c.c. respectively) were mixed and boiled for 2 hours. The solution was then treated as before, and the solid residue, recrystallised from a large volume of alcohol, gave *tri*-o-*anisylphosphine*-p-*toluenesulphonylimine*, m. p. 273—274° (Found: C, 64·6; H, 5·5; N, 2·7. $C_{28}H_{28}O_5NSP$ requires C, 64·45; H, 5·4; N, 2·7%).

(*b*) The solution resulting from the reaction of this type was finally evaporated to half bulk. On cooling, a large crop of the phosphinimine crystallised out; this was removed, and

the filtrate evaporated to dryness. The residue was extracted with hot benzene, and the solution, filtered from undissolved phosphinimine, deposited *hydroxytri*-o-*anisylphosphine*-p-*toluenesulphonamide*, which when recrystallised from benzene had m. p. 149° (Found: C, 62·2; H, 5·6; N, 2·7. $C_{28}H_{30}O_6NSP$ requires C, 62·3; H, 5·6; N, 2·6%).

The preparation of the phosphine oxide was attempted by the usual method of bromination followed by alkaline hydrolysis; the product, recrystallised from aqueous alcohol, proved to be *tribromotri*-o-*anisylphosphine oxide*, m. p. 245° (Found: C, 41·95; H, 3·1; Br, 39·3. $C_{21}H_{18}O_3Br_3P$ requires C, 41·7; H, 3·0; Br, 39·6%). The method of preparation shows that the bromine atoms are in the benzene ring and not in the methoxyl group; it is probable that the *m*-directing influence of the phosphorus atom reinforces the *o*-directing influence of the methoxyl group, and the groups P, OMe, and Br are in the 1, 2, and 3 positions respectively.

Tri-p-*anisylphosphine* was similarly prepared from *p*-bromoanisole, but after hydrolysis a portion of the phosphine had separated from the ether, whilst the rest remained dissolved in the ether and was recovered; recrystallisation from alcohol gave the pure phosphine, m. p. 131° (Found: C, 71·7; H, 6·0%).

(*a*) The phosphine was treated as before with anhydrous chloramine-T in absolute alcohol, and the residue, recrystallised from alcohol, gave *tri*-p-*anisylphosphine*-p-*toluenesulphonylimine*, m. p. 155° (Found: C, 64·4; H, 5·2; N, 2·6%).

(*b*) In order to determine whether the crude product obtained under conditions (*b*) was homogeneous, one portion was recrystallised from benzene, another from ethyl carbonate, and the remainder from carbon tetrachloride. Each solvent, however, furnished solely the *hydroxytri*-p-*anisylphosphine*-p-*toluenesulphonamide*, m. p. 121° (Found: C, 62·1; H, 5·6; N, 2·6%). No phosphinimine could be detected.

Tri-m-*anisylphosphine* was prepared similarly to the *p*-isomeride, part of the crude phosphine again separating from the ether and the remainder being recovered from the ethereal solution. Recrystallisation from alcohol gave the pure phosphine, m. p. 115° (Found: C, 71·4; H, 5·9%).

(*a*) Solutions of the phosphine (4 g.) and anhydrous chloramine-T (2·6 g.) in hot absolute alcohol (100 c.c. and 30 c.c. respectively) were mixed, the heat of the reaction causing the solvent to boil. The mixture was treated as before, but the final residue formed a thick viscous syrup; this, when kept for several days in a vacuum, solidified to a brittle glass, but neither the syrup nor the glass could be purified by recrystallisation. When the syrup was stirred with water, it was rapidly converted into the hydroxy-sulphonamide described below; if even traces of water were present in the initial reaction mixture, this was again obtained.

(*b*) Similar experiments but of this type gave a final residue, which rapidly solidified and when recrystallised from benzene afforded *hydroxytri*-m-*anisylphosphine*-p-*toluenesulphonamide*, m. p. 112° (Found: C, 62·1; H, 5·55; N, 2·7%). This compound is unstable in alcoholic or carbon tetrachloride solution, and recrystallisation from these solvents furnished *tri*-m-*anisylphosphine oxide*, m. p. 151—152° (Found: C, 68·2; H, 5·6. $C_{21}H_{21}O_4P$ requires C, 68·5; H, 5·7%). When, however, equimolecular quantities of the oxide and of *p*-toluenesulphonamide were dissolved in hot benzene, the pure hydroxy-sulphonamide again separated on cooling.

The Trischlorophenylphosphines.—These three phosphines were prepared by the action of phosphorus trichloride or tribromide on a Grignard reagent prepared from the corresponding chloroiodobenzene. The first experiments, however, furnished solely the corresponding phosphine oxides, owing to the fact that oxidation occurs very readily during the preparation, although the tertiary phosphines when isolated and purified are not readily oxidised. The difficulty was finally overcome by carrying out the entire preparation and subsequent hydrolysis in an atmosphere of hydrogen as before, and then blowing the reaction mixture by means of the compressed hydrogen directly from the apparatus through a delivery tube into a separating-funnel filled with carbon dioxide. When the aqueous layer had been removed, the ethereal solution was run into a conical flask containing sodium sulphate and previously filled with carbon dioxide; two delivery tubes (similar to those of a wash-bottle) were then fitted to the flask and closed. A small Buchner funnel, having a sintered-glass filter-plate, was fitted into the main neck of a suitable Claisen distilling-flask, and the funnel closed by a cork pierced by a delivery tube joined to the outlet tube of the conical flask. The dried ethereal solution was then slowly blown by compressed carbon dioxide over into the funnel, and the clear filtrate thus transferred to the distilling-flask without exposure to the air. The ether was distilled off, and the residue heated to 260° under reduced pressure in an atmosphere of hydrogen to remove by-products. The final residue was chilled whilst still exposed to hydrogen, and was then extracted with a minimum of hot alcohol, an insoluble viscous syrup remaining. In the case of all three chlorophenylphosphines, crystallisation occurred very slowly from the first alcoholic

extract, and was sometimes delayed for several days; subsequent recrystallisations occurred with increasing rapidity as the product became purer.

Tri-o-chlorophenylphosphine.—Concentrated hydrochloric acid (400 c.c.) was added in small quantities (*ca.* 20 c.c.) at a time to a mixture of *o*-chloronitrobenzene (126 g.) and granular tin (180 g.) contained in a large flask fitted with a reflux condenser. The mixture was occasionally shaken until the addition was complete, and was then heated on a water-bath for 2 hours, and finally made alkaline and steam-distilled. The *o*-chloroaniline was extracted with ether and obtained as an oil, b. p. 98—100°/20 mm. If an excess of hydrochloric acid is added during the reduction, the main product is 2 : 4-dichloroaniline (cf. Blanksma, *Rec. trav. chim.*, 1906, **25**, 368).

o-Chloroaniline (200 g.) was dissolved in a mixture of water (1200 c.c.) and concentrated hydrochloric acid (270 c.c.) at 70°. A further 270 c.c. of acid were then added, and the solution vigorously stirred whilst being chilled to − 5° to precipitate fine crystals of the hydrochloride. Sodium nitrite (110 g.) in water (250 c.c.) was then added, and the diazo-solution added in turn to potassium iodide (400 g.) dissolved in water (400 c.c.), a vigorous reaction ensuing. The mixture was then heated on a water-bath for 2 hours. The dark heavy oil was separated, added to 33% sodium hydroxide solution (200 c.c.), and steam-distilled. The *o*-chloroiodobenzene had b. p. 226—228°. Klages and Liecke (*J. pr. Chem.*, 1900, **61**, 321) gave b. p. 234—235°

The phosphine was then prepared by the action of a solution of phosphorus trichloride (12·8 g.) in ether (50 c.c.) on a Grignard reagent prepared from magnesium (10·2 g.) and *o*-chloroiodobenzene (100 g.) in ether (200 c.c.). The chilled product was hydrolysed with a solution of ammonium chloride (50 g.) in water (250 c.c.), and finally worked up as described above. The *tri-o-chlorophenylphosphine*, when recrystallised from absolute alcohol, had m. p. 185° (Found : C, 58·9; H, 3·3; Cl, 29·2. $C_{18}H_{12}Cl_3P$ requires C, 59·1; H, 3·3; Cl, 29·1%); the yield was always low.

(*a*) Solutions of the phosphine (1 g.) and anhydrous chloramine-T (0·65 g.) in hot absolute alcohol (50 and 20 c.c. respectively) were mixed and then treated as before. Crystals separated whilst the final solution was evaporating in the desiccator. The oily residue, when recrystallised from alcohol, gave *tri-o-chlorophenylphosphine-p-toluenesulphonylimine*, m. p. 235—236° (Found : C, 56·0; H, 3·85; N, 2·7; Cl, 20·0. $C_{25}H_{19}O_2NCl_3SP$ requires C, 56·1; H, 3·6; N, 2·6; Cl, 19·9%).

(*b*) A similar experiment with hydrated chloramine-T in rectified spirit again gave the phosphinimine, no other product being detected.

Tri-o-chlorophenylphosphine oxide, $P(C_6H_4Cl)_3O,\frac{1}{2}H_2O$, was prepared by the usual method of bromine addition followed by hydrolysis, and also as a by-product in the first attempted preparations of the phosphine. Recrystallised from glycol monoethyl ether, the oxide formed beautiful leaflets, m. p. 226—236° (Found : H, 3·5; Cl, 27·3. $C_{18}H_{12}OCl_3P,\frac{1}{2}H_2O$ requires H, 3·4; Cl, 27·3%. Consistent values for carbon could not be obtained by micro- or macro-analysis).

All attempts made to unite the oxide and *p*-toluenesulphonamide in various solvents failed, the components being recovered unchanged.

Tri-p-chlorophenylphosphine.—The reduction of *p*-chloronitroaniline, unlike that of the *o*-compound, is not affected by an excess of acid. The nitro-compound (150 g.) was therefore dissolved in a hot mixture of water (450 c.c.), alcohol (800 c.c.), and concentrated hydrochloric acid (1100 c.c.) contained in a 5-litre flask fitted with a reflux condenser. Granular tin (180 g.) was added over a period of 1 hour, and the solution then boiled for at least 5 hours. Steam-distillation removed the alcohol, and then, when the solution was made alkaline, the *p*-chloroaniline, which was purified by recrystallisation from aqueous alcohol.

A solution of *p*-chloroaniline (100 g.) in a warm mixture of water (300 c.c.) and concentrated hydrochloric acid (300 c.c.) was cooled to 10° and diazotised with sodium nitrite (56 g.) in water (120 c.c.). The diazo-solution was added to potassium iodide (200 g. in 400 c.c. of water) as before, and the *p*-chloroiodobenzene isolated by steam-distillation. It was purified by distillation; m. p. 56°, b. p. 102—103°/12 mm.

Tri-p-chlorophenylphosphine, prepared as for the *o*-isomeride, had m. p. 103° after recrystallisation from absolute alcohol (Found : C, 59·4; H, 3·3; Cl, 29·0%).

(*a*) The phosphine, when treated as usual under these conditions, gave a product which rapidly crystallised during the evaporation. Recrystallisation of the crude dry product from much absolute alcohol gave *tri-p-chlorophenylphosphine-p-toluenesulphonylimine*, m. p. 232° (Found : C, 56·3; H, 3·8; N, 2·7; Cl, 19·9%).

(*b*) When the phosphine in rectified spirit was boiled with hydrated chloramine-T, and the

solution then slowly evaporated to dryness, crystals of m. p. 115—116° were obtained. These may have been a very unstable hydroxy-sulphonamide. When they were repeatedly recrystallised from benzene containing about 10% of *cyclo*hexane, pure *p*-toluenesulphonamide, m. p. and mixed m. p. 137—138°, was obtained; the filtrate from the first recrystallisation, when evaporated to dryness and recrystallised from ethyl carbonate, gave *tri*-p-*chlorophenylphosphine oxide*, m. p. 175° (Found: Cl, 27·7. $C_{18}H_{12}OCl_3P$ requires Cl, 27·9%). When an alcoholic solution of the oxide and of *p*-toluenesulphonamide was boiled, no combination could be detected; a portion of the residue obtained by complete evaporation gave the oxide on recrystallisation from ethyl carbonate, and the remainder gave the unchanged sulphonamide from benzene. It is noteworthy that the phosphinimine was also obtained when the phosphine was treated with *hydrated* chloramine-T in absolute alcohol; its formation is therefore not inhibited by *small* quantities of water.

Tri-m-*chlorophenylphosphine*.—*m*-Chloroaniline, *m*-chloroiodobenzene, and this *phosphine* were prepared similarly to the *o*-isomerides. The last compound, when recrystallised from alcohol, had m. p. 67° (Found: C, 59·1; H, 3·3; Cl, 28·9%). The yield of the *p*- and the *m*-chloro-phosphine was always considerably higher than that of the *o*-compound.

(*a*) The phosphine, by the usual procedure, gave finally a white solid residue. The only suitable solvent found for purification was rectified spirit, from which the residue on repeated recrystallisation gave tri-*m*-chlorophenylphosphine oxide, m. p. 135° (Found: Cl, 27·5. Calc. for $C_{18}H_{12}OCl_3P$: Cl, 27·9%). Challenger and Wilkinson (*loc. cit.*) gave the same m. p.

(*b*) Under these conditions, the phosphine furnished a solid residue which, when recrystallised from either alcohol or ethyl carbonate, gave only the above oxide.

A solution of tri-*m*-nitrophenylphosphine oxide (1 g.) and *p*-toluenesulphonamide (0·42 g.) in acetone (150 c.c.) was boiled under reflux for 30 minutes and then evaporated to 50 c.c.; on cooling, the unchanged phosphine oxide crystallised out. Similar solutions were prepared in dioxan (30 c.c.) and also in glycol monoethyl ether (35 c.c.) and boiled as before; on cooling (without concentration) the unchanged oxide separated in each case.

Phenyldimethylphosphine.—A mixture of benzene (275 g.), phosphorus trichloride (400 g.), and aluminium chloride (60 g.) was boiled under reflux for 50 hours; the whole of the liquid product was then distilled off and finally fractionated under reduced pressure, the resulting phenyldichlorophosphine having b. p. 105—107°/23 mm. Phenyldimethylphosphine was then prepared by the action of the dichloro-phosphine (25 g.) in ether (50 c.c.) on a Grignard reagent prepared from magnesium (12·1 g.) and methyl iodide (71 g.) in ether (150 c.c.); it had b. p. 82°/20 mm. Meisenheimer (*Annalen*, 1926, **449**, 227) gives b. p. 83—84°/13·5 mm.

(*a*) Solutions of the freshly distilled phosphine (2 g.) and anhydrous chloramine-T (3·3 g.), each in hot absolute alcohol (20 c.c.), were mixed, the usual precipitation of sodium chloride immediately occurring. Evaporation finally gave a mobile oil, which refused to solidify, and from which no crystalline product could be obtained.

(*b*) These conditions also afforded a mobile oil, which dissolved readily in cold benzene, and did not therefore contain free *p*-toluenesulphonamide. Since, however, the oil could not be directly recrystallised, it was extracted with a hot mixture of carbon tetrachloride and benzene. The solution deposited an oil, which solidified after several days. It was then recrystallised from benzene–*cyclo*hexane, and *p*-toluenesulphonamide, m. p. 137—138°, was ultimately obtained. The mother-liquors undoubtedly contained the very soluble phenyldimethylphosphine oxide.

Phenyldiethylphosphine.—Prepared as for the dimethyl compound, but from ethyl iodide (78 g.), the phosphine had b. p. 108—109°/20 mm. Meisenheimer (*loc. cit.*) gives b. p. 96—98°/10 mm. The phosphine, when treated with chloramine-T under either conditions (*a*) or (*b*), gave *phenyldiethylphosphine*-p-*toluenesulphonylimine*, m. p. 82° after recrystallisation from alcohol (Found: C, 61·2; H, 6·6; N, 4·2. $C_{17}H_{22}O_2NSP$ requires C, 60·9; H, 6·6; N, 4·2%).

By similar methods were prepared *p*-tolyldichlorophosphine (Michaelis and Paneck, *Annalen*, 1882, **212**, 206) [toluene (300 g.), phosphorus trichloride (400 g.), aluminium chloride (60 g.)], b. p. 122—125°/21 mm., and *p*-tolyldimethylphosphine, b. p. 93—95°/12 mm. This phosphine, when treated with chloramine-T under conditions (*a*) and (*b*), gave results similar to those of the phenyl compound, no phosphinimine or stable hydroxy-sulphonamide being isolated.

p-Tolyldiethylphosphine, prepared similarly to the phenyl compound, had b. p. 114—115°/12 mm. Treatment of the freshly distilled phosphine with chloramine-T under conditions (*a*) or (*b*) gave p-*tolyldiethylphosphine*-p-*toluenesulphonylimine*, m. p. 120° after recrystallisation from alcohol (Found: C, 62·3; H, 6·9; N, 4·0. $C_{18}H_{24}O_2NSP$ requires C, 61·9; H, 6·9; N, 4·0%).

It is probable from these results that a methyl group attached to the phosphorus atom inhibits hydroxy-sulphonamide formation: similar results were obtained with the arsines (Mann, *loc. cit.*).

The following *trialkylphosphine*-p-*toluenesulphonylimines* were prepared by method (*a*); evaporation in a desiccator gave a mobile oil which usually did not solidify until it was exposed to the air and scratched with a rod: *triethyl* compound, m. p. 119° from alcohol (Found: C, 54·6; H, 7·5; N, 5·1. $C_{13}H_{22}O_2NSP$ requires C, 54·3; H, 7·7; N, 4·9%); *tri*-n-*propyl* compound, m. p. 66° from ether (Found: C, 58·1; H, 8·5; N, 4·2. $C_{16}H_{28}O_2NSP$ requires C, 58·3; H, 8·55; N, 4·25%); *tri*-n-*butyl* compound, m. p. 54° from *cyclo*hexane (Found: C, 61·8; H, 9·1; N, 3·9. $C_{19}H_{34}O_2NSP$ requires C, 61·4; H, 9·2; N, 3·8%). The solubilities of the alkyl compounds in the usual organic solvents increase rapidly as the homologous series is ascended. Treatment of the propyl- and the butyl-phosphine with hydrated chloramine-T gave semi-solid products from which no pure crystalline compound was isolated.

Triphenylarsine-p-*toluenesulphonylimine*.—Solutions of triphenylarsine (3 g.) and anhydrous chloramine-T (2·3 g.), each in absolute alcohol (30 c.c.), were mixed and treated as usual. The final residue rapidly solidified, and on recrystallisation from absolute alcohol gave the *arsinimine*, m. p. 192—193° (Found: H, 4·6; N, 3·0; S, 6·5. $C_{25}H_{22}O_2NSAs$ requires H, 4·65; N, 2·95; S, 6·7%. Consistent values for C could not be obtained).

The *tri*-o-*tolylarsine*-p-*toluenesulphonylimine*, similarly obtained from tri-o-tolylarsine (2·0 g.) and anhydrous chloramine-T (1·3 g.), each in 40 c.c. of absolute alcohol, and recrystallised from absolute alcohol, had m. p. 201—202° (Found: C, 65·2; H, 5·5; N, 2·8. $C_{28}H_{28}O_2NSAs$ requires C, 64·9; H, 5·45; N, 2·7%). The *tri*-p-*tolylarsinimine*, similarly obtained and recrystallised, had m. p. 185° (Found: C, 65·1; H, 5·6; N, 2·8%).

A similar experiment performed with tri-*m*-tolylarsine gave a viscous oil which did not solidify for several days, and then formed a waxy solid from which no crystalline derivative could be obtained.

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