

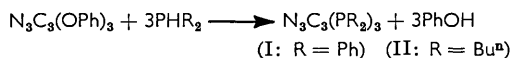
197. 1,3,5-Triazines. Part IV.¹ Phosphino-1,3,5-triazines.

By W. HEWERTSON, R. A. SHAW, and B. C. SMITH.

Phosphino-1,3,5-triazines have been prepared by three different methods, and their reactions have been studied. Addition of methyl iodide, oxygen, sulphur, or selenium occurs under suitable conditions, and some metal complexes of trisdiphenylphosphino-1,3,5-triazine (I) have been prepared. Cleavage of the phosphorus-triazine bond occurs on bromination, oxidative hydrolysis, or treatment with an excess of methyl iodide. Phosphinotriazines are compared with phosphines containing P-acyl, P-P, and P-Ge bonds.

THIS Paper describes the preparation and properties of a new class of compounds, phosphino-1,3,5-triazines. Three methods of preparation have been developed successfully: (a) reaction of a secondary phosphine with triphenyl cyanurate; (b) reaction of a secondary phosphine with cyanuric chloride in aqueous acetone, followed by treatment with an inorganic base; and (c) reaction of a secondary phosphine with a chlorotriazine under anhydrous conditions. Analogous methods are used in the preparation of amino-1,3,5-triazines (substituted melamines).² Three general methods of preparation of tertiary phosphines are unsuitable for the preparation of 2,4,6-trisdiphenylphosphino-1,3,5-triazines: (d) decomposition of triazine quaternary phosphonium salts; (e) reaction of metal derivatives of diphenylphosphine with cyanuric chloride; and (f) reaction of organo-metallic compounds with chlorophosphines.

(a) Secondary phosphines (3 moles) react with triphenyl cyanurate at 200° in the absence of solvent. Reaction occurs by aryloxy-triazine fission rather than aryl-oxygen fission. Phenol is evolved, and 2,4,6-trisphosphino-1,3,5-triazines are obtained in excellent (>80%) yields. 2,4,6-Trisdiphenylphosphino-1,3,5-triazine (I) is a colourless



crystalline solid which is stable in air. 2,4,6-Trisdi-n-butylphosphino-1,3,5-triazine (II), a colourless viscous oil, which is oxidised in air and is more difficult to isolate. Cyclotriphosphazatrienes show certain chemical similarities to 1,3,5-triazines,³ but no reaction was observed on heating diphenylphosphine with hexaphenoxycyclotriphosphazatriene at 300° for 4 hours.

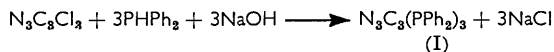
(b) Reaction of diphenylphosphine (3 moles) with a suspension of cyanuric chloride in aqueous acetone at 0°, followed by neutralisation with sodium hydroxide, gives the

¹ Part III, Hewertson, Shaw, and Smith, *J.*, 1963, 1670.

² Smolin and Rapoport, "s-Triazines and Derivatives," Interscience, New York and London, 1958.

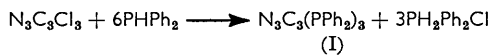
³ Fitzsimmons and Shaw, *Proc. Chem. Soc.*, 1961, 258; Shaw, Fitzsimmons, and Smith, *Chem. Rev.*, 1962, 62, 247.

trisphosphine (I) in 65% yield. The attempted preparation of 2,4-dichloro-6-diphenyl-



phosphino-1,3,5-triazine by this method was unsuccessful. It is probable that the phosphinodichlorotriazine undergoes self-quaternisation to oligomeric or polymeric products, analogous to that reported for bromoethylethylphenylphosphine, which gives 1,4-diethyl-1,4-diphenyldiethylenediphosphonium dibromide.⁴

(c) Reaction of diphenylphosphine (6 moles) with cyanuric chloride in boiling benzene gives a precipitate of diphenylphosphonium chloride, and the trisphosphine (I) is obtained in 57% yield.



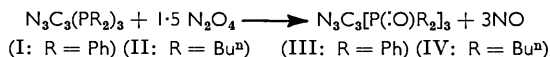
Reaction of diphenylphosphine (2 moles) with 2-chloro-4,6-diphenyl-1,3,5-triazine at 100° in the absence of solvent gives 2-diphenylphosphino-4,6-diphenyl-1,3,5-triazine in 75% yield. Some hydrogen chloride is evolved during both reactions, but at least two equivalents of phosphine per mole of chloro-compound appear to be necessary. The use of tertiary amines as hydrogen-halide acceptors was avoided because of possible reaction with cyanuric chloride.⁵ One mole of hydrogen chloride was evolved during the reaction of diphenylphosphine (3 moles) with cyanuric chloride in xylene at 50–60°. Only a trace (<0.1%) of the trisphosphine (I) was obtained. Diphenylphosphine (3 moles) was heated with cyanuric chloride in boiling benzene, and then at 150° in the absence of solvent. Only 2 moles of hydrogen chloride were evolved, and the trisphosphine (I) was not obtained.

(d) Thermal or hydrolytic cleavage of phosphonium salts proceeds by fission of the phosphorus-triazine bond, and phosphinotriazines have not been prepared by this route. Methyl-diphenylphosphine (3 moles) dissolves cyanuric chloride at 130°, and the mixture begins to char at 170°, but methyl chloride is not evolved. Triphenylphosphine and cyanuric chloride give a quaternary salt, presumably $\text{N}_3\text{C}_3(\text{PPh}_3)_3\text{Cl}_3$, from which triphenylphosphine sublimates at 150° at atmospheric pressure. The salt reacts with hydroxylic solvents to give triphenylphosphine and cyanuric acid. Heating of the trisphosphine (I) with an excess of methyl iodide gives dimethyldiphenylphosphonium iodide.

(e) Issleib and Priebe⁶ prepared acylphosphines by reaction of alkali-metal derivatives of secondary phosphines with acyl halides. Cyanuric chloride resembles acyl halides,^{1,7} but attempts to prepare phosphino-derivatives of 1,3,5-triazine were unsuccessful. A study of reactions of monochlorotriazines with metal diphenylphosphides would be of value.

(f) Organometallic derivatives of 1,3,5-triazines are unknown.

Reactions of Phosphinotriazines.—Oxidation. The trisphosphines (I) and (II) are oxidised to the corresponding tris(phosphine oxides) (III) and (IV) by dinitrogen tetroxide in cyclohexane.



The quantity of dinitrogen tetroxide required by this equation is consumed, although nitric oxide can oxidise certain phosphines.⁸ Tertiary phosphines have been oxidised by an excess of dinitrogen tetroxide in the absence of solvent,⁹ but phosphinotriazines give tarry products under these conditions. The tris(phosphine oxides) (III and IV) have also been prepared by the Arbusov reaction.¹

⁴ Hitchcock and Mann, *J.*, 1958, 2081.

⁵ Golesworthy, Shaw, and Smith, *J.*, 1962, 1507; Kober and Rätz, *J. Org. Chem.*, 1962, 27, 2510.

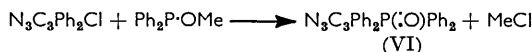
⁶ Issleib and Priebe, *Chem. Ber.*, 1959, 92, 3183.

⁷ Hewertson, Shaw, and Smith, *J.*, 1962, 3267.

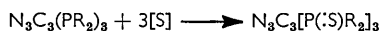
⁸ Cadogan, *Quart. Rev.*, 1962, 16, 208.

⁹ Addison and Sheldon, *J.*, 1956, 2705.

The tris(phosphine oxide) (III) hydrolyses in air to give cyanuric acid and diphenylphosphinic acid.¹ A solution of 2-diphenylphosphino-4,6-diphenyl-1,3,5-triazine (V) in ethanol was oxidised by air to the phosphine oxide, $N_3C_3Ph_2P(:O)Ph_2$ (VI). The greater hydrolytic stability of compound (VI) depends on the greater resistance of C-2 of the triazine ring to nucleophilic attack because of replacement of electron-withdrawing 4,6-phosphinoxyl by phenyl groups.¹ The phosphine oxide (VI) has been prepared also by an Arbuzov reaction between methyl diphenylphosphinite and 2-chloro-4,6-diphenyl-1,3,5-triazine.

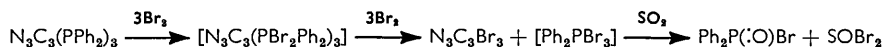


Addition of sulphur takes place without side-reactions when the trisphosphines (I) and (II) are heated with sulphur in benzene.

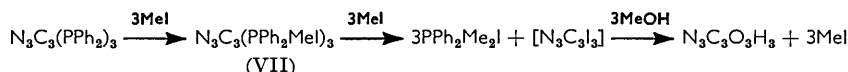


Selenium reacts less readily to form the compound $N_3C_3[P(:Se)Ph_2]_3$.

With bromine. Titration of bromine against the trisphosphine (I) in methylene chloride under an atmosphere of nitrogen indicates reaction of four bromine atoms per phosphorus atom. Treatment of the reaction mixture with dry sulphur dioxide gives cyanuric bromide and diphenylphosphinyl bromide. Similar reaction in air gives a lachrymatory oil from which diphenylphosphinic acid was isolated. The following reaction scheme is suggested.



With methyl iodide. Reaction of methyl iodide (3 moles) with the trisphosphine (I) in benzene at room temperature gives low yields of the tris(phosphine methiodide), $N_3C_3(PPh_2MeI)_3$ (VII), and a red oil which reacts with methanol to give cyanuric acid. Pure cyanuric iodide has not yet been prepared but cyanuric chloride and bromide give cyanuric acid on treatment with methanol.² Further reaction of the methiodide (VII) gives dimethyldiphenylphosphonium iodide. The methiodide (VII) is stable to boiling methanol and the following reaction scheme is proposed.



Formation of co-ordination compounds. The trisphosphine (I) reacts with mercuric iodide (3 moles) to form a stable co-ordination compound which is insufficiently soluble for molecular weight determinations. The compound is represented as a derivative of three-co-ordinate mercury, but the fourth co-ordination position in the solid state may well be occupied by bridging iodine atoms.¹⁰



Reaction of the trisphosphine (I) with chromium hexacarbonyl in boiling diethylene glycol dimethyl ether gives a tris(pentacarbonylchromium(0) complex, $N_3C_3[PPh_2, Cr(CO)_5]_3$.

The above results make it clear that the trisphosphine (I) differs considerably from triphenylphosphine. Chloro-1,3,5-triazines are known to resemble acyl chlorides^{1,7} and, more generally, the triazine ring resembles inorganic and organic acid residues. Phosphino-1,3,5-triazines, $N_3C_3(PR_2)_2$, can therefore be compared with acylphosphines, diphosphines, cyclophosphines, and related compounds, *e.g.*, $R_2P \cdot GrR'_3$. Methyl iodide formed addition compounds with acylphosphines,⁵ addition or cleavage occurs with

¹⁰ Cf. Cass, Coates, and Hayter, *J.*, 1955, 4007.

diphosphines and cyclotetraphosphines,¹¹⁻¹⁵ and diphenyl(triethylgermyl)phosphine¹⁶ gives triethyliodogermane and dimethyldiphenylphosphonium iodide. Detailed work with phosphinotriazines shows that the addition compound is easily cleaved by an excess of methyl iodide, and it seems likely that addition precedes cleavage in all these systems. Similar reactions with molecular halogens lead to cleavage of the relevant P-P^{12,14,17,18} P-Ge,¹⁶ and P-triazine bonds.

Under anhydrous conditions, trivalent phosphorus in some acylphosphines⁶ and diphosphines^{14,18} is oxidised to the phosphine oxide, whilst in diphenyl(triethylgermyl)phosphine¹⁶ the bonds are cleaved. With phosphino-1,3,5-triazines, it was found that oxidation to quinquevalent phosphorus or cleavage depends on the choice of oxidising agent, the stoichiometry, and the reaction conditions. The addition of sulphur to trivalent phosphorus occurs in phosphinotriazines and some diphosphines.^{13,14,18} Whilst varying degrees of susceptibility to hydrolysis have been reported^{11,17,19,20} all the relevant bonds undergo oxidative hydrolytic cleavage to give acidic fragments from both parts of the molecule.^{5,18} Although all these classes of compound have moderate thermal stability^{18,20} they are less stable than tertiary phosphines.

Adjacent acyl, phosphino-, germyl, and triazino-groups probably weaken, but do not destroy, the donor properties of phosphino-groups, and complexes are formed.^{5,12,17,18,21}

EXPERIMENTAL

Cyanuric chloride was recrystallised from carbon tetrachloride, and triphenylphosphine from ethanol. Organic solvents were dried by conventional methods. Reactions were carried out under an atmosphere of nitrogen unless stated otherwise. Cold air-free water was used for hydrolysis.

Phosphines.—*Diphenylphosphine.* Diphenylphosphine was prepared from triphenylphosphine by the method of Hewertson and Watson.²²

Methyldiphenylphosphine. Triphenylphosphine (26.2 g., 0.1 mole) was added to a solution of sodium (4.6 g., 0.2 mole) in liquid ammonia (200 ml.). The orange solution was treated with dry ammonium bromide²² (9.8 g., 0.1 mole) and methyl iodide (14.2 g., 0.1 mole), the ammonia was allowed to evaporate, and the residue was hydrolysed with water and extracted with ether (3 × 50 ml.). Distillation of the dried ether solution gave methyldiphenylphosphine (17.7 g., 88%), b. p. 111–112°/0.15 mm. (lit.,²³ 120–122°/0.2 mm.).

Di-n-butylphosphine. Dry phosphine, prepared from zinc phosphide and dilute sulphuric acid, was bubbled through a solution of sodium (25.3 g., 1.1 mole) in liquid ammonia (1 l.) until the colour changed from blue to pale green. n-Butyl bromide (137 g., 1 mole) was added, and followed after 30 min. by sodamide, prepared from sodium (23 g., 1 mole), in liquid ammonia (500 ml.). Further n-butyl bromide (123 g., 0.9 mole) was added until the green colour was discharged. The mixture was hydrolysed with ether saturated with water. The ammonia was allowed to evaporate and the residue was washed with water (33 ml.), extracted with ether (2 × 500 ml.), and dried (Na₂SO₄). Distillation at atmospheric pressure gave di-n-butylphosphine (76.4 g., 57.7%), b. p. 183–186° (lit.,²⁴ 184–186°).

2,4,6-Trisdiphenylphosphino-1,3,5-triazine (I).—(a) *From triphenyl cyanurate.* Triphenyl cyanurate⁷ (8.92 g., 0.025 mole) and diphenylphosphine (13.95 g., 0.075 mole) were heated at 210–220° (3 hr.) and then at 250° (1 hr.). Phenol was evolved, and the residue was held at

¹¹ Hoffmann, Grünwald, and Horner, *Chem. Ber.*, 1960, **93**, 861.

¹² Issleib and Mitcherling, *Z. Naturforsch.*, 1960, **15b**, 267.

¹³ Issleib and Jacob, *Chem. Ber.*, 1961, **94**, 107.

¹⁴ Issleib and Seidel, *Chem. Ber.*, 1959, **92**, 2681.

¹⁵ Issleib and Tzschach, *Chem. Ber.*, 1960, **93**, 1852.

¹⁶ Glockling and Hooton, *Proc. Chem. Soc.*, 1963, 146.

¹⁷ Issleib and Seidel, *Z. anorg. Chem.*, 1960, **303**, 155.

¹⁸ Kuchen and Buchwald, *Chem. Ber.*, 1958, **91**, 2871.

¹⁹ Kosolapoff, "Organophosphorus Compounds," Wiley, New York, 1950, p. 14.

²⁰ Reetz, Chadwick, Hardy, and Kaufman, *J. Amer. Chem. Soc.*, 1955, **77**, 3813; Buckler, *J. Org. Chem.*, 1959, **24**, 1460.

²¹ Issleib and Schwager, *Z. anorg. Chem.*, 1961, **310**, 43; 1961, **311**, 83.

²² Hewertson and Watson, *J.*, 1962, 1490.

²³ Trippett and Walker, *J.*, 1961, 1266.

²⁴ Issleib and Tzschach, *Chem. Ber.*, 1959, **92**, 704.

150°/10 mm. to remove the remaining phenol. The product solidified on trituration with boiling methanol. Recrystallisation from benzene-ethanol gave the *product* (I) (15.2 g., 96%), m. p. 143–144° (Found: C, 73.9; H, 4.8; N, 6.6; P, 14.1%; *M*, 627. $C_{30}H_{30}N_3P_3$ requires C, 73.9; H, 4.8; N, 6.6; P, 14.7%; *M*, 634), ν_{\max} . (KBr) 3080, 1460, 1430, 1245, 1100, 1065, 1025, 740, and 695 cm^{-1} .

(b) *From cyanuric chloride in aqueous acetone.* Cyanuric chloride (6.1 g., 0.033 mole) in acetone (50 ml.) was added to stirred ice-water (*ca.* 100 g.). Diphenylphosphine (18.6 g., 0.1 mole) in acetone (20 ml.) was added slowly (15 min.) to the resulting suspension at 0–5°. A pale green colour appeared; the mixture was heated at 100° ($\frac{1}{2}$ hr.), cooled, and neutralised with dilute sodium hydroxide solution; a sticky green mass was formed which was insoluble in the aqueous phase but dissolved in benzene (2 \times 50 ml.). The reaction mixture was exposed to air and the organic layer was filtered and evaporated, to give an oil which crystallised on trituration with methanol. Passage through a short silica gel column gave the trisphosphine (I) (13.7 g., 65%), m. p. and mixed m. p. 142–144° (from benzene-ethanol).

Reaction of diphenylphosphine (11 g., 0.059 mole) with cyanuric chloride (10.9 g., 0.059 mole) in acetone (50 ml.) and water (125 ml.) at 0°, and addition of sodium hydrogen carbonate (4.15 g., 0.048 mole) gave a pale green oil which was extracted with benzene. Attempted short-path distillation was unsuccessful, and the residue became a gummy paste. A black hygroscopic solid was formed on exposure to air.

(c) *From cyanuric chloride in benzene.* Diphenylphosphine (58 g., 0.31 mole) in dry benzene (100 ml.) was added slowly (20 min.) to a stirred solution of cyanuric chloride (9.2 g., 0.05 mole) in benzene (100 ml.). The solution became lime-yellow and was boiled under reflux (24 hr.); a sticky precipitate formed, and hydrogen chloride was evolved. The solution was filtered, and evaporation gave an oil which crystallised on standing. The solid product, washed with methanol, gave the trisphosphine (I) (18.2 g., 57.4%), m. p. and mixed m. p. 143–144° (from benzene-ethanol).

Hydrogen chloride (0.035 mole) was evolved during reaction of diphenylphosphine (18.6 g.) with cyanuric chloride (6.1 g., 0.033 mole) in xylene (130 ml.) at 50–60° (2 hr.). Potassium carbonate (8.6 g., 0.06 mole) was added, and a trace of the trisphosphine (I) (35 mg.) was isolated from the yellow oily mixture. The main product was an unidentified hygroscopic solid containing nitrogen and phosphorus, but not chlorine, with ν_{\max} . 730 and 691 cm^{-1} (cf. phenyl), and 1720 and 1440 cm^{-1} (cf. cyanuric acid).

Hydrogen chloride (total 0.02 mole) was evolved during reaction of diphenylphosphine (5.6 g., 0.03 mole) with cyanuric chloride (1.84 g., 0.01 mole), first in boiling benzene (6 hr.) and then in the absence of solvent at 150° (2 hr.). The product dissolved in ethanol and a precipitate of silver chloride was formed on treatment of a sample with ethanolic silver nitrate. A brown gum was formed on addition of benzene to the ethanol solution. The trisphosphine (I) was not obtained.

(d) *Reactions of cyanuric chloride with tertiary phosphines.* Cyanuric chloride (1.84 g., 0.01 mole) in ether (70 ml.) was added slowly to a stirred solution of triphenylphosphine (7.86 g., 0.03 mole) in ether (100 ml.) at 0°. The white amorphous precipitate, m. p. >340°, was filtered in air and washed with ether. Attempted recrystallisation of a sample from cold ethanol-ether gave cyanuric acid, and triphenylphosphine was obtained from the filtrate. Attempted sublimation of the remainder at 150°/11 mm. gave triphenylphosphine (6.1 g.).

Cyanuric chloride (2.3 g., 0.0125 mole) and methyl-diphenylphosphine (7.1 g., 0.0475 mole) were heated in the absence of solvent. The solid product darkened at 100° and charred at 170°. Methyl chloride was not evolved and no other volatile products were obtained.

(e) *Reaction of cyanuric chloride with metal diphenylphosphides.* Reaction of cyanuric chloride (3.0 g., 0.017 mole) with an ether solution of sodium diphenylphosphide, prepared from sodium (1.15 g., 0.05 mole) and diphenylphosphine (9.3 g., 0.05 mole) in liquid ammonia, deposited a red gum. Evaporation of the ether and extraction with benzene gave a red tarry product containing Cl, N, Na(trace), and P. The trisphosphine (I) was not obtained.

A similar product was obtained from reaction, in tetrahydrofuran at –30 to –40°, of cyanuric chloride (3.0 g., 0.017 mole) with diphenylphosphinolithium, prepared from diphenylphosphine (10.2 g., 0.055 mole) and an excess of lithium. A similar product was obtained from reaction of cyanuric chloride (3.0 g., 0.017 mole) in benzene-ether with diphenylphosphino-magnesium bromide prepared from magnesium (1.2 g., 0.05 mole), bromobenzene (8.0 g., 0.05 mole), and diphenylphosphine (9.3 g., 0.05 mole).

Reactions of 2,4,6-Trisdiphenylphosphino-1,3,5-triazine (I).—Oxidation. 2,4,6-Trisdiphenylphosphino-1,3,5-triazine (I) (0.63 g., 1 mmole) in cyclohexane (10 ml.) was treated with a standard solution of dinitrogen tetroxide (0.138 g., 1.5 mmole) in cyclohexane. Recrystallisation of the colourless precipitate from chloroform–light petroleum (b. p. 60–80°) gave 2,4,6-trisdiphenylphosphinyl-1,3,5-triazine (III),¹ m. p. and mixed m. p. 243–245°.

The trisphosphine (I) (0.63 g., 1 mmole) and sulphur (0.1 g., 3 mmole) in benzene (20 ml.) were boiled under reflux (2.5 hr.). Recrystallisation of the resulting yellow solid from benzene gave 2,4,6-trisdiphenylphosphinothioyl-1,3,5-triazine (0.64 g., 90%), m. p. 223–225° (Found: C, 64.45; H, 4.4; N, 6.2; S, 13.2. $C_{39}H_{30}N_3P_3S_3$ requires C, 64.2; H, 4.1; N, 5.8; S, 13.2%).

The trisphosphine (I) (0.32 g., 0.5 mmole) reacted similarly with freshly distilled selenium (0.22 g., 2.4 mmoles), and recrystallisation of the product from benzene gave orange cubes of 2,4,6-trisdiphenylphosphinoselenoyl-1,3,5-triazine (0.27 g., 57%), m. p. 232–234° (Found: P, 10.4. $C_{39}H_{30}N_3P_3Se_3$ requires P, 10.7%).

With bromine. The trisphosphine (I) (3.17 g., 0.005 mole) in methylene chloride (150 ml.) consumed 44.1 ml. of a 10.65% solution of bromine in methylene chloride (3.87 atoms of Br per atom of P). The mixture, which contained a pale yellow solid, was treated with dry sulphur dioxide and the solvent was evaporated. The residue was heated at 50°/1 mm. (1 hr.) to remove thionyl bromide. Extraction of the resulting oily solid with light petroleum (b. p. 60–80°) left a colourless solid. Sublimation at 100–120°/0.1 mm. gave cyanuric bromide (0.93 g., 56.7%), m. p. 262.5–265° (lit.,² 264–265°). Removal of the solvent and short-path distillation of the residue gave diphenylphosphinic bromide (2.12 g., 49%), b. p. 120–125°/0.25 mm. (Found: Br, 28.2. Calc. for $C_{12}H_{10}BrOP$: Br, 28.5%).

A solution of bromine (1.3 g., 0.008 mole) in chloroform (15 ml.) reacted immediately when added to a cooled solution of the trisphosphine (I) (1.58 g., 0.025 mole) in air. The resulting pale yellow solution was treated with ether (30 ml.) and the lachrymatory oil which was deposited solidified on washing with water (0.5 ml.), giving diphenylphosphinic acid (1.03 g., 65%), m. p. and mixed m. p. 197–199° (from benzene and ether–ethanol) (Found: C, 66.1; H, 5.5. Calc. for $C_{12}H_{11}O_2P$: C, 66.0; H, 5.1%).

With methyl iodide. A solution of the trisphosphine (I) (3.17 g., 0.005 mole) in boiling benzene (15 ml.) was treated with an excess of methyl iodide (4 ml.) and methanol (1 ml.). An oil settled from the boiling solution after 30 min., and a brown solid was formed on cooling. Extraction with boiling methanol, and addition of ether gave dimethyldiphenylphosphonium iodide (4.8 g., 93%), m. p. 250–251° (from ethanol) (Found: C, 49.5; H, 5.0; P, 8.7. Calc. for $C_{14}H_{10}IP$: C, 49.1; H, 4.7; P, 9.05%). This was characterised further by preparation of dimethyldiphenylphosphonium picrate, m. p. 119–121° (Found: C, 53.8; H, 4.5; N, 9.3; P, 7.0. $C_{20}H_{16}N_3O_7P$ requires C, 54.2; H, 4.1; N, 9.5; P, 7.0%).

The trisphosphine (I) (3.17 g., 0.005 mole) in benzene (50 ml.) was treated with methyl iodide (2.13 g., 0.015 mole). A red oil separated during 2 days. Extraction with boiling benzene (300 ml.), addition of ether, and recrystallisation from methanol–ether gave pale yellow needles of 2,4,6-trisdiphenylphosphino-1,3,5-triazine trismethiodide (VII) (1.43 g., 22%), m. p. 246–248° (Found: C, 47.7; H, 3.45; I, 36.0. $C_{42}H_{39}I_3N_3P_3$ requires C, 47.6; H, 3.7; I, 35.9%). The remaining oil was extracted with boiling methanol, and cyanuric acid (0.34 g.) was deposited from the cooled solution. The trismethiodide (VII) was recovered after boiling in methanol whereas reaction with an excess of methyl iodide in boiling methanol gave dimethyldiphenylphosphonium iodide.

Formation of co-ordination compounds. Mercuric iodide (1.36 g., 0.03 mole) in hot ethanol (100 ml.) was added to a solution of the trisphosphine (I) (0.63 g., 0.01 mole) in hot ethanol (125 ml.). The resulting yellow precipitate was washed with ethanol, and recrystallisation from benzene (500 ml.) gave 2,4,6-trisdiphenylphosphino-1,3,5-triazine tris(mercuric iodide) (1.43 g., 72%), m. p. 216–218° (Found: C, 23.6; H, 1.5; Hg, 30.7; I, 38.4. $C_{39}H_{30}Hg_3I_6N_3P_3$ requires C, 23.4; H, 1.5; Hg, 30.1; I, 38.1%).

Chromium hexacarbonyl (1.32 g., 0.06 mole) and the trisphosphine (I) (1.27 g., 0.02 mole) in diethylene glycol dimethyl ether (40 ml.) were heated at 120° for 1.5 hr. The resulting yellow solid, on recrystallisation from chloroform–ethanol, gave 2,4,6-trisdiphenylphosphino-1,3,5-triazine tris(pentacarbonylchromium(0)) (1.86 g., 72%), m. p. >300° (Found: C, 53.6; H, 2.3; P, 7.5. $C_{54}H_{30}Cr_3N_3O_{15}P_3$ requires C, 53.6; H, 2.5; P, 7.7%).

2,4,6-Trisdi-n-butylphosphino-1,3,5-triazine (II).—Triphenyl cyanurate (17.8 g., 0.05 mole) and di-n-butylphosphine (21.9 g., 0.15 mole) were heated at 200–220° (4 hr.). Phenol, b. p.

48–50°/1 mm., was removed by distillation, and the residual oil was washed with methanol and dried *in vacuo*. Repeated molecular distillation (path length 0.5 cm.) gave the *product* (II) (21.3 g., 83%) as a colourless viscous oil, b. p. 115°/0.01 mm., n_D^{25} 1.5160 (Found: C, 62.7; H, 10.3; N, 7.9. $C_{27}H_{54}N_3P_3$ requires C, 63.4; H, 10.6; N, 8.2%).

The trisphosphine (II) (2.2 g.) in cyclohexane (50 ml.) was treated with a standard solution of dinitrogen tetroxide (0.37 g., 0.04 mole) in cyclohexane. The solvent was removed, and recrystallisation of the residue gave 2,4,6-tris(di-*n*-butylphosphinyl)-1,3,5-triazine (IV) (1.91 g., 79%), m. p. 248–250°, identical with a sample prepared by the Arbuzov reaction.¹

Reaction of the trisphosphine (II) (0.43 g., 0.083 mole) and sulphur (0.1 g., 0.003 mole) in boiling benzene (20 ml.), evaporation of solvent, and recrystallisation from light petroleum (b. p. 60–80°) gave needles of 2,4,6-tris(di-*n*-butylphosphinothiyl)-1,3,5-triazine (0.41 g., 80%), m. p. 127–129° (Found: C, 52.8; H, 8.8; N, 7.0; P, 15.4; S, 16.3. $C_{27}H_{54}N_3P_3S_3$ requires C, 53.0; H, 8.9; N, 6.9; P, 15.2; S, 15.8%).

2-Diphenylphosphino-4,6-diphenyl-1,3,5-triazine (V).—Nitrogen was bubbled through a mixture of diphenylphosphine (1.2 g., 6.4 mole) and 2-chloro-4,6-diphenyl-1,3,5-triazine (0.86 g., 3.2 mole) at 100°; hydrogen chloride was evolved. The mixture solidified on cooling. Trituration with light petroleum (b. p. 60–80°) gave the *product* (V) (1.04 g., 74.5%), m. p. 130–132° (from benzene-ethanol and ethanol) (Found: C, 77.6; H, 4.7; N, 9.9; P, 7.5. $C_{27}H_{30}N_3P$ requires C, 77.7; H, 4.8; N, 10.1; P, 7.4%). The mother-liquors were exposed to air and evaporated to dryness. Recrystallisation from ethanol gave 2-diphenylphosphinyl-4,6-diphenyl-1,3,5-triazine (VI) (0.16 g., 12%), m. p. 175–176° (Found: C, 74.9; H, 4.8; N, 9.9; P, 6.7. $C_{27}H_{30}N_3OP$ requires C, 74.8; H, 4.65; N, 9.7; P, 7.15%). A strong P=O band occurs at 1215 cm^{-1} . The phosphine oxide (VI) was obtained also by reaction of 2-chloro-4,6-diphenyl-1,3,5-triazine (2.67 g., 0.01 mole) with methyl diphenylphosphinite (2.16 g., 0.01 mole) in boiling benzene (20 ml.). Methyl chloride was evolved, the solvent was evaporated, and recrystallisation from ethanol gave (VI) (3.7 g., 84%), m. p. and mixed m. p. 175–176°.

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