313. 1,3,5-*Triazines. Part III.*[1] *Arbuzov Reactions of Chlorotriazines.*

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Arbuzov reactions of chloro-1,3,5-triazines with phosphorus(III) alkyl esters give triazino-derivatives of phosphorus(V). The relative ease of replacement of chlorine in 4,6-disubstituted 2-chloro-1,3,5-triazines is discussed in terms of the electron-withdrawing effect of the 4,6-substituents, and of groups X in the esters $X_2P{\cdot}OR$. The products are less stable to heat and hydrolysis than are corresponding benzene derivatives.

Reaction of cyanuric chloride with trialkyl phosphites to give 2,4,6-trisdialkoxyphosphinyl-1,3,5-triazines (I) and alkyl chlorides has been reported by Coover[2] and Morrison:[3]

$$N_3C_3Cl_3 + 3P(OR)_3 \longrightarrow \underset{\text{(I)}}{N_3C_3[PO(OR)_2]_3} + 3RCl$$

2-Chloro-4,6-bistrichloromethyl-1,3,5-triazine is reported to react with triethyl phosphite.[4] Further Arbuzov reactions of chloro-1,3,5-triazines with phosphorus(III) esters are described in this paper.

Cyanuric chloride resembles acyl chlorides rather than alkyl chlorides.[1] Vigorous reaction occurs at room temperature in the absence of solvent with trialkyl phosphites, and competitive side reactions are not observed. Reaction takes place conveniently in a boiling solvent, *e.g.*, benzene or xylene, and its progress may be followed by collecting the eliminated alkyl chloride in a graduated cold trap. Reaction with alkyl diphenyl phosphites requires concentrated solutions or absence of solvent. Arbuzov and Nesterov[5] have reported that these phosphites are less reactive than trialkyl phosphites towards alkyl halides. Cyanuric chloride does not undergo the reported[2] Arbuzov reaction with triphenyl phosphite, but above 200° triphenyl cyanurate and diphenyl phosphorochloridite are formed.[1] Quasi-phosphonium addition compounds of alkyl halides with triphenyl phosphite are decomposed by alcohols, to give diphenyl alkylphosphonates,[6] but the phenyl ester (I; R = Ph) could not be prepared by this method and was obtained on reaction of cyanuric chloride with methyl or ethyl diphenyl phosphite. No reaction occurred between cyanuric chloride and methyl *o*-phenylene phosphite at 110° in 24 hr.; tarry decomposition products were formed above 110°, but methyl chloride was not evolved. No reaction was observed between cyanuric chloride and methyl phosphorodichloridite, $Cl_2P{\cdot}OMe$.

The methyl,[3] ethyl,[2,3] isopropyl, and phenyl esters (I) are colourless and crystalline, the n-butyl and benzyl esters (I) were viscous undistillable oils. The Michaelis reaction of cyanuric chloride with sodium dibutyl phosphite gave low yields of the butyl ester as an oil, but this method is less convenient than the Arbuzov reaction. The methyl, ethyl, and isopropyl esters are reasonably stable to atmospheric hydrolysis but the phenyl ester cannot be recrystallised in air from dried hydrocarbon solvents—its preparation by a Michaelis reaction, and purification by washing with an aqueous solution, were reported[2] but the compound was not characterised. The liquid esters decompose when kept in air and amorphous solid products are deposited. Analyses and infrared spectra indicate decomposition of the triazine ring and it is presumed that pyrophosphonates are formed.

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[1] Part II, Hewertson, Shaw, and Smith, *J.*, 1962, 3267.
[2] Coover, U.S.P. 2,685,581/1958.
[3] Morrison, *J. Org. Chem.*, 1957, **22**, 444.
[4] Schroeder, *J. Amer. Chem. Soc.*, 1959, **81**, 5658.
[5] Arbuzov and Nesterov, *Izvest. Akad. Nauk S.S.S.R., Otdel khim. Nauk*, 1954, 427; *Chem. Abs.*, 1955, **49**, 9541c.
[6] Landauer and Rydon, *J.*, 1953, 2224; Arbuzov and Nesterov, *Bull. Akad. Sci. U.S.S.R.*, 1954, 361.

The parent acid $N_3C_3[PO(OH)_2]_3$ has not been obtained. The esters decompose above 200° in an atmosphere of nitrogen. Dialkyl alkylphosphonates, $R'\cdot PO(OR)_2$ ($R > Me$), decompose thermally to give olefins and the corresponding phosphonic acid.[7] The ethyl ester (I; R = Et) gave approximately six mol. of ethylene but the residue decomposed further and the acid was not obtained.

The relative ease of nucleophilic replacement of the 2-chloro-atom in 1,3,5-triazines depends on the nature of the 4,6-substituents, and decreases in the order of decreasing electron-withdrawing effect, *viz.*, Cl, $CCl_3 > Ph >$ piperidino. 2-Chloro-4,6-bistrichloromethyl-1,3,5-triazine reacts with triethyl phosphite at 0°.[4] The 6-phenyl and the 4,6-diphenyl derivatives require bath-temperatures of 110—115° and 145—150°, respectively, before evolution of ethyl chloride occurs. Reaction of the 6-piperidino- and 4,6-dipiperidino-derivatives with triethyl phosphite in the absence of solvent require, respectively, 1 hr. at 140—145° and 2½ hr. at 150°. Electron-withdrawing substituents, *e.g.*, Cl, reduce the electron density on the triazine ring which then becomes more susceptible to nucleophilic attack. Electron-releasing substituents, *e.g.*, piperidino, increase the electron density of the triazine ring which becomes less susceptible to nucleophilic attack. The phosphonate derivatives, $N_3C_3X[PO(OR)_2]_2$ (II) and $N_3C_3X_2\cdot PO(OR)_2$ (III) [(*a*) X = $C_5H_{10}N$, R = Et; (*b*) X = Ph, R = Me or Et], obtained by reaction of chloro-1,3,5-triazines with trialkyl phosphites, are crystalline solids which are reasonably stable in air.

Partial replacement of chlorine has not been studied in detail. Reaction of cyanuric chloride (1 mol.) with trimethyl phosphite (2 mol.) in benzene gives the methyl ester (I; R = Me) in 64% yield, and cyanuric chloride (32%) is recovered. This appears to confirm the assumption that phosphonate groups withdraw electrons [8] from the triazine ring, although an excess of cyanuric chloride (10 mol.) reacts with triethyl phosphite to give a monophosphonate derivative. The monophosphonate $N_3C_3Cl_2\cdot PO(OEt)_2$ was not isolated but reaction with an excess of piperidine gave 2-diethoxyphosphinyl-4,6-dipiperidino-1,3,5-triazine (III*a*). This compound was also obtained, but in low yield, from a similar reaction of cyanuric chloride (1 mol.) and triethyl phosphite (2 mol.) followed by reaction with piperidine, but 80% of the products of this reaction were unidentified. The trisphosphonate derivative (I; R = Et) does not react with piperidine under these conditions.

The Arbuzov reaction has been extended to reactions of cyanuric chloride with other phosphorous esters. The reactivity of compounds $X_2P\cdot OAlk$ decreases in the order X = Alk, Ph > OAlk > OPh > Cl, which is the order of increasing electron-withdrawing effect. Reaction with diethyl phenylphosphonite, $Ph\cdot P(OEt)_2$, takes place in boiling benzene and ethyl chloride is evolved more rapidly than in reactions with triethyl phosphite. The crystalline product, 2,4,6-tri[ethoxy(phenyl)phosphinyl]-1,3,5-triazine, is stable in air and decomposes above 200°. Reaction takes place immediately on addition of cyanuric chloride to dilute solutions of ethyl dibutylphosphinite, $Bu^n{}_2P\cdot OEt$, and ethyl diphenylphosphinite, $Ph_2P\cdot OEt$, in benzene. The phosphine oxide products are more stable thermally than the phosphonates and phosphinates. The trisdiphenylphosphinyl derivative, $N_3C_3(POPh_2)_3$, decomposes above 300°, hence is less stable thermally than triphenylphosphine oxide. The compound is hydrolysed easily, and attempted recrystallisation from ethanol in air gives cyanuric acid and diphenylphosphinic acid:

$$N_3C_3(POPh_2)_3 \longrightarrow N_3C_3O_3H_3 + 3Ph_2PO_2H$$

EXPERIMENTAL

Cyanuric chloride was recrystallised from carbon tetrachloride, dried *in vacuo*, and stored under nitrogen. Trialkyl phosphites were distilled immediately before use. Reactions were carried out in an atmosphere of dry nitrogen. Organic solvents were dried and purified by conventional methods. Light petroleum was of b. p. 60—80° unless stated otherwise.

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[7] Canavan, Dowden, and Eaborn, *J.*, 1962, 331.

[8] Freedman and Jaffé, *J. Amer. Chem. Soc.*, 1955, **77**, 920.

Tribenzyl phosphite, b. p. 184—186°/0·01 mm., n_D^{25} 1·5694 (lit.,[10] n_D^{25} 1·5695), was prepared from phosphorus trichloride, benzyl alcohol, and pyridine in ether by Ramirez's method.[9] Other phosphites were prepared by reaction of the appropriate phosphorochloridite with alcohol and *NN*-diethylaniline in ether. Diphenyl phosphorochloridite, b. p. 120—122°/0·6 mm., n_D^{25} 1·5776, prepared from triphenyl phosphite and propionyl chloride,[1] was used in the preparation of methyl diphenyl phosphite, b. p. 112—118°/1·5 mm. (lit.,[5] 165·5—166·5°/12 mm.), and ethyl diphenyl phosphite, b. p. 126—133°/0·8 mm. (lit.,[5] 182—183°/17·5 mm.). The preparation of methyl *o*-phenylene phosphite, b. p. 82—83°/12 mm. (lit.,[10] 73°/8 mm.), from *o*-phenylene phosphorochloridite [11] and methanol was preferred to the preparation from methyl phosphorodichloridite [12] and pyrocatechol.

TABLE 1.

Reactions of cyanuric chloride with alkyl phosphites.

	Phosphite (g.)	$N_3C_3Cl_3$ (g.)	Solvent	(ml.)	Bath-temp.	Time (hr.)	Alkyl halide (g.)	Alkyl halide (%)	Phosphonate (g.)	Phosphonate (%)
1 $(MeO)_3P$	19·2	9·2	Benzene	50	100—110°	2	5·7	75	19·0	94
2 $(EtO)_3P$	25·7	9·2	Benzene	60	100—110	2	8·6	89	22·1	93
3 $(Pr^iO)_3P$	15·6	4·6	Toluene	80	130—140	1·5	4·7	82	10·6	74
4 $(Bu^nO)_3P$	18·8	4·6	Xylene	100	145—150	1	6·4	92	13·5	81
5 $(Ph{\cdot}CH_2{\cdot}O)_3P$ ...	13·2	2·3	None *		100	1	4·0	84	7·3	68
6 $MeO{\cdot}P(OPh)_2$ ...	18·6	4·6	Benzene	20	105—110	3	3·1	82	13·6	70
7 $EtO{\cdot}P(OPh)_2$ ...	26·2	6·1	Benzene	70	105—115	6	3·4	55	14·8 †	57
8 $MeO{\cdot}P(O_2C_6H_4)$	10·2	3·7	None		105—110	24	0	0	0	0
9 $MeO{\cdot}PCl_2$	10·0	4·6	None		100—110	5	0	0	0	0

* Mixture heated at 11 mm. to assist removal of benzyl chloride, b. p. 65°/11 mm. † Phenyl ester not obtained crystalline from this reaction.

Preparation of 2,4,6-*Trisdialkoxyphosphinyl*-1,3,5-*triazines* (I).—Reaction conditions are recorded in Table 1. Solutions of phosphite were added dropwise to stirred solutions of cyanuric chloride. Heating was continued until the volume of alkyl chloride, collected in a cooled (−80°) graduated flask, remained constant for ½ hr. The reflux condenser was maintained at a temperature above the b. p. of eliminated alkyl chloride. Analytical data and m. p.s of 2,4,6-*trisdialkoxyphosphinyl*-1,3,5-*triazines* are recorded in Table 2. The methyl ester crystallised on cooling; the ethyl ester crystallised on addition of cyclohexane; the isopropyl ester was obtained first as an oil which crystallised from light petroleum solution at −80°; the phenyl ester was obtained first as an oil which crystallised on trituration with light petroleum; the n-butyl and benzyl esters were not obtained crystalline and could not be distilled at 0·01 mm.; they were purified by repeated deposition from solution, and were dried *in vacuo.*

TABLE 2.

2,4,6-Trisdialkoxyphosphinyl-1,3,5-triazines.

R in $N_3C_3[PO(OR)_2]_3$	M. p.	Recryst. from *	Found (%)				Formula	Required (%)			
			C	H	N	P		C	H	N	P
1 Me	124—125° †	C_6H_6	26·3	4·6	10·3	22·7	$C_9H_{18}N_3O_9P_3$ ‡	26·7	4·5	10·4	22·9
2 Et	95—96 §	C_6H_6–C_6H_{12}	37·0	6·2	8·9	19·6	$C_{15}H_{30}N_3O_9P_3$	36·8	6·2	8·6	19·0
3 Pr^i	67—70	Et_2O–Pet	44·0	6·9	6·9	15·8	$C_{21}H_{42}N_3O_9P_3$	43·95	7·4	7·3	16·2
4 Bu^n	Oil ¶	Pet	49·0	8·1	6·4	13·7	$C_{27}H_{54}N_3O_9P_3$	49·3	8·3	6·4	14·1
5 $PhCH_2$.........	Oil **	C_6H_6–Pet	61·4	4·8	5·1	10·3	$C_{45}H_{42}N_3O_9P_3$	62·7	4·9	4·9	10·8
6 Ph	94—95	,,	59·4	3·8	5·3	12·4	$C_{39}H_{30}N_3O_9P_3$	60·2	3·9	5·4	12·0

* Pet = light petroleum. † Lit.,[3] m. p. 123—124·5. ‡ Found: *M*, 428. Calc.: *M*, 405. § Lit.,[2] m. p. 82—84°; [3] m. p. 94—95°; ¶ n_D^{25} 1·4390. ** n_D^{25} 1·5802.

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[9] Ramirez, personal communication.

[10] Kosolapoff, " Organo-Phosphorus Compounds," John Wiley and Sons, New York, 1950, p. 205.

[11] Anschütz, Broeker, Neher, and Ohnheiser, *Chem. Ber.*, 1943, **76**, 218.

[12] Martin and Pizzolato, *Inorg. Synth.*, 1953, **4**, 63.

No reaction occurred with methyl *o*-phenylene phosphite. Cyanuric chloride sublimed on attempted distillation of methyl *o*-phenylene phosphite, but an excess of piperidine added to the reaction mixture in benzene (100 ml.) gave 2,4,6-tripiperidino-1,3,5-triazine (5·25 g., 82·5%), and methyl *o*-phenylene phosphite (8·7 g., 85%) was recovered. No reaction occurred with methyl phosphorodichloridite. Cyanuric chloride (4·1 g., 90%) and lower yields of methyl phosphorodichloridite (6·3 g., 63%) were recovered.

Michaelis Reaction.—A stirred solution of cyanuric chloride (4·6 g., 0·025 mole) and sodium di-n-butyl phosphite, prepared from di-n-butyl phosphite (14·4 g., 0·075 mole) and sodium (1·72 g., 0·075 mole), in ether (200 ml.) was boiled under reflux for 24 hr. Sodium chloride was removed by filtration, and evaporation gave a straw-coloured oil which was redeposited from light petroleum (b. p. 40—60°). The product was washed with light petroleum at low temperature, dried *in vacuo* (60°, 3 hr.), and identified as 2,4,6-trisdi-n-butoxyphosphinyl-1,3,5-triazine (7·83 g., 47·2%), n_D^{25} 1·4388.

Attempted Preparation of 2,4,6-*Trisdiphenoxyphosphinyl*-1,3,5-*triazine* (I; R = Ph) *from Cyanuric Chloride, Triphenyl Phosphite, and Butan*-1-*ol.*—Triphenyl phosphite (23·3 g., 0·075 mole) and cyanuric chloride (4·6 g., 0·025 mole) in decalin (10 ml.) were heated at 160—180° (1 hr.) and cooled. Butan-1-ol (5·55 g., 0·075 mole) was added and the solution was boiled under reflux at 140—148° for 1 hr. The colourless solid which was deposited was filtered off, washed with ether, and identified as cyanuric acid (2·83 g., 87·7%), m. p. >300° (sublimes), by its infrared spectrum. The volatile fraction of the filtrate distilled when heated slowly to 40°/2 mm., and was collected in a cold trap, washed with water, and dried. Redistillation gave butyl chloride (6·1 g., 88%). Distillation of the residual oil gave a forerun, b. p. 150—205°/2 mm. (1·7 g.), and triphenyl phosphite (19·8 g., 85%), b. p. 205—208°/2 mm., was recovered. The residue solidified when washed with ether, and recrystallisation from benzene gave triphenyl cyanurate (0·83 g., 9·2%), identical with a sample prepared previously.[1]

This experiment indicates that rapid decomposition to triphenyl cyanurate and diphenyl phosphorochloridite occurs at the temperature required to form an adduct between triphenyl phosphite and cyanuric chloride. n-Butyl chloride is obtained by two reactions (2 and 3):

$$\text{(1)}\quad N_3C_3Cl_3 + (PhO)_3P \longrightarrow N_3C_3(OPh)_3 + (PhO)_2PCl \quad \text{(ref. 1}$$

$$\text{(2)}\quad (PhO)_2PCl + Bu^nOH \longrightarrow (PhO)_2P{\cdot}OH + Bu^nCl \quad \text{(cf. ref. 13)}$$

$$\text{(3)}\quad N_3C_3Cl_3 + Bu^nOH \longrightarrow N_3C_3O_3H_3 + Bu^nCl \quad \text{(ref. 14)}$$

Thermal Decomposition of 2,4,6-*Trisdiethoxyphosphinyl*-1,3,5-*triazine* (I; R = Et).—Gas evolved from the phosphonate (0·98 g., 0·002 mole) was passed into a solution of bromine (0·96 g., 0·012 mole) in chloroform (20 ml.). The colour paled progressively to yellow and it was estimated that 95% of the bromine was decolorised. The solution was washed with dilute hydroxylamine hydrochloride solution and water, and dried ($CaCl_2$); gas–liquid chromatography (15% Apiezon " L " on Celite 72/85 mesh) at 98° showed two peaks having relative retention times of 7·80. A 5% solution of a known sample of ethylene dibromide in chloroform had relative retention times of 7·83. In a second experiment the phosphonate (227·0 mg.) was heated in a porcelain crucible on a thermogravimetric balance. Weight loss began at 190° and was complete at 200° (40 min.). The loss in weight was 79·6 mg. (calc. for 6 mol. of ethylene: 78·0 mg.). The residue was a crisp brown foam which became gummy in air.

Partial Replacement of Chlorine.—(*a*) Triethyl phosphite (16·6 g., 0·1 mole) in benzene was added dropwise in 1 hr. to a stirred solution of cyanuric chloride (9·2 g., 0·05 mole) in boiling benzene (50 ml.). Ethyl chloride (5·5 g., 78·5%) was evolved for 1 hr., then the solvent was evaporated. Attempted distillation of the residual oil at 135—140°/0·01 mm. caused decomposition. Addition of piperidine (8·5 g., 0·1 mole) to a solution of the oil in benzene (100 ml.) at 0° gave a precipitate of piperidine hydrochloride. The mixture was boiled for 1 hr., cooled, and filtered. Evaporation of the filtrate gave an oil which crystallised from dioxan on addition of water. Further recrystallisation gave 2-*diethoxyphosphinyl*-4,6-*dipiperidino*-1,3,5-*triazine* (3·73 g., 19·5%) (III*a*), m. p. 104—107° (Found: C, 53·4; H, 7·6; N, 17·6; P, 8·3. $C_{17}H_{30}N_5O_3P$ requires C, 53·25; H, 7·9; N, 18·3; P, 8·1%).

[13] Ref. 10, p. 182.

[14] Klason, *J. prakt. Chem.*, 1886, **34**, 152.

(*b*) Triethyl phosphite (8·3 g., 0·05 mole) in benzene (20 ml.) was added dropwise in ½ hr. to a stirred solution of cyanuric chloride (92 g., 0·5 mole) in boiling benzene (200 ml.) and light petroleum (b. p. 80—100°) (200 ml.). The mixture was boiled under reflux for 1 hr., solvents were evaporated, and cyanuric chloride (80·4 g., 0·437 mole) was removed by sublimation at 90°/0·5 mm. for 5 hr. Treatment of the residual oil with piperidine in benzene as before gave 2-diethoxyphosphinyl-4,6-dipiperidino-1,3,5-triazine (14·7 g., 77%), m. p. and mixed m. p. 105—107°. The samples had identical infrared spectra.

(*c*) Similar reactions of trimethyl phosphite (12·4 g., 0·1 mole) in benzene (20 ml.) with cyanuric chloride (9·2 g., 0·05 mole) gave methyl chloride (4·5 g., 82%) and colourless crystals of 2,4,6-trisdimethoxyphosphinyl-1,3,5-triazine (I; R = Me) (10·6 g., 64%), m. p. and mixed m. p. 124—125° (from benzene). Evaporation of the mother-liquor gave cyanuric chloride (2·94 g., 32%).

Preparation of 6-*Substituted* 2,4-*Bisdialkoxyphosphinyl*-1,3,5-*triazines* (II).—2,4-Dichloro-6-phenyl-1,3,5-triazine was prepared by the method of Hirt *et al.*[15] 2,4-*Dichloro*-6-*piperidino*-1,3,5-*triazine*, m. p. 88—90°, b. p. 140—142°/1 mm., prepared from cyanuric chloride (18·4 g., 0·1 mole), piperidine (8·5 g., 0·1 mole), and 2N-sodium hydroxide (50 ml.) in aqueous dioxan suspension at −5°, was purified by distillation (Found: C, 41·5; H, 4·5; N, 24·5; Cl, 30·0. $C_8H_{10}Cl_2N_4$ requires C, 41·2; H, 4·3; N, 24·0; Cl, 30·4%).

TABLE 3.

Reactions of substituted chlorotriazines with trialkyl phosphites.

	Phosphite	Phosphite (g.)	$N_3C_3XCl_2$ X	(g.)	Bath-temp.	Time (hr.)	Alkyl halide (g.)	(%)	Phosphonate (g.)	(%)
10	$(MeO)_3P$ ...	5·0	Ph	4·52	120—135°	1 *	1·60	80	5·7	76
11	$(EtO)_3P$ ...	6·7	Ph	4·53	110—115	3 †	2·16	82	6·2	72
12	$(EtO)_3P$ ...	8·3	$C_5H_{10}N$	5·8	140	1 *	2·45	77	7·3	67
			$N_3C_3X_2Cl$							
13	$(MeO)_3P$ ...	3·7	Ph	2·67	135—140	1·5 *	0·40	80	2·76	81
14	$(EtO)_3P$ ...	3·3	Ph	2·67	145—150	1 *	0·51	83	2·9	78
15	$(EtO)_3P$ ...	3·3	$C_5H_{10}N$	2·81	150	2·5 *	0·48	75	2·5	66

* Without solvent. † In 10 ml. of benzene.

TABLE 4.

2-Mono- and 2,4-bis-dialkoxyphosphinyl-1,3,5-triazines.

	Phosphonate	M. p.	Recryst. from *	Found (%) C	H	N	P	Formula	Required (%) C	H	N	P
10	$N_3C_3Ph[PO(OMe)_2]_2$	114—116°	C_6H_6–C_6H_{12} †	41·8	4·3	10·8	16·8	$C_{13}H_{17}N_3O_6P_2$	41·8	4·6	11·3	16·6
11	$N_3C_3Ph[PO(OEt)_2]_2$	61—63	C_6H_6–Pet ‡	47·5	6·1	9·5	14·6	$C_{17}H_{25}N_3O_6P_2$	47·6	5·9	9·8	14·4
12	$N_3C_3(NC_5H_{10})[PO(OEt)_2]_2$	68—70	subln.§	44·2	6·5	12·6	14·5	$C_{16}H_{30}N_4O_6P_2$	44·0	6·9	12·8	14·2
13	$N_3C_3Ph_2PO(OMe)_2$	125—126	C_6H_{12}	59·6	4·6	12·5	9·3	$C_{17}H_{16}N_3PO_3$	59·8	4·7	12·3	9·1
14	$N_3C_3Ph_2PO(OEt)_2$	98—99·5	Pet	61·7	5·4	11·4	8·5	$C_{19}H_{20}N_3PO_3$	61·8	5·5	11·4	8·4
15	$N_3C_3(NC_5H_{10})_2PO(OEt)_2$	104—106	Aq. dioxan	¶								

* Pet = light petroleum. † Repeated recrystalln. required. ‡ Oil eluted previously with benzene on silica column. § Oil triturated previously with light petroleum at −40°; subln. at 190°/0·01 mm. ¶ Identified by m. p., mixed m. p., and infrared spectrum.

Conditions of reaction of dichlorotriazines with trialkyl phosphites are recorded in Table 3. Analytical data and m. p.s of 6-substituted 2,4-*bisdialkoxyphosphinyl*-1,3,5-*triazines* are recorded in Table 4.

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[15] Hirt, Nidecker, and Berchtold, *Helv. Chim. Acta*, 1950, **33**, 1365.

Preparation of 4,6-*Disubstituted* 2-*Dialkoxyphosphinyl*-1,3,5-*triazines* (III).—2-Chloro-4,6-diphenyl-1,3,5-triazine was prepared by the method of Hirt *et al.*[15] and 2-chloro-4,6-dipiperidino-1,3,5-triazine by that of Pearlman and Banks.[16] Conditions of reaction with trialkyl phosphites are recorded in Table 3. Analytical data and m. p.s of 4,6-disubstituted 2-*dialkoxyphosphinyl*-1,3,5-*triazines* are recorded in Table 4.

2,4,6-*Tri[ethoxy(phenyl)phosphinyl]*-1,3,5-*triazine*.—Diethyl phenylphosphonite, b. p. 77°/1·2 mm. (lit.,[17] b. p. 110—111°/10—13 mm.), was prepared from dichlorophenylphosphine, ethanol, and *NN*-diethylaniline in ether. Reaction of diethyl phenylphosphinite (14·8 g., 0·075 mole) and cyanuric chloride (4·6 g., 0·025 mole) in boiling benzene (75 ml.) and evaporation of the solvent gave an oil which was triturated with light petroleum (4 × 20 ml.), and crystallisation from benzene gave a solid, m. p. 114—121°. Further purification by elution down an activated charcoal column and recrystallisation from benzene gave 2,4,6-*tri[ethoxy(phenyl)phosphinyl]*-1,3,5-*triazine* (3·6 g., 35%), m. p. 120—121° (Found: C, 55·8; H, 5·4; N, 7·4; P, 15·8. $C_{27}H_{30}N_3O_6P_3$ requires C, 55·4; H, 5·2; N, 7·2; P, 15·9%).

2,4,6-*Trisdi-n-butylphosphinyl*-1,3,5-*triazine*.—Ethyl di-n-butylphosphinite, b. p. 97—98°/12 mm. (lit.,[18] b. p. 112—116°/15 mm.), was prepared from chlorodi-n-butylphosphine.[19] Cyanuric chloride (4·6 g., 0·025 mole) in benzene (100 ml.) was added dropwise (20 min.) to a stirred solution of the phosphinite (14·2 g., 0·075 mole) in benzene (125 ml.) at 0°, giving a pale yellow waxy solid precipitate. Next morning the supernatant liquid was decanted, and the residue was washed with " AnalaR " acetone. Recrystallisation from benzene and " AnalaR " acetone gave 2,4,6-*trisdi-n-butylphosphinyl*-1,3,5-*triazine* (9·0 g., 64%), m. p. 249—250° (Found: C, 57·7; H, 9·35; N, 7·6; P, 16·8. $C_{27}H_{54}N_3O_3P_3$ requires C, 57·7; H, 9·7; N, 7·5; P, 16·5%). Addition of a solution of cyanuric chloride to ethyl di-n-butylphosphinite at room temperature gave the trisphosphine oxide (7·85 g., 56%), isolated as before. Ethyl chloride (4·35 g., 90%) was not evolved until the mixture was heated to 65°.

2,4,6-*Trisdiphenylphosphinyl*-1,3,5-*triazine*.—Methyl diphenylphosphinite, b. p. 128°/2 mm. (lit.,[18] b. p. 151—152°/10 mm.), was prepared from chlorodiphenylphosphine. Cyanuric chloride (3·7 g., 0·02 mole) in benzene (40 ml.) was added dropwise in 1 hr. to a stirred solution of the phosphinite (13·0 g., 0·06 mole) in benzene (100 ml.). Next morning the precipitate was filtered off and washed with benzene. Recrystallisation from chloroform–light petroleum (b. p. 60—80°) and " AnalaR " acetone gave 2,4,6-*trisdiphenylphosphinyl*-1,3,5-*triazine* (11·2 g., 65%), m. p. 243—245° (Found: C, 68·5; H, 4·2; N, 6·2; P, 13·35. $C_{39}H_{30}N_3O_3P_3$ requires C, 68·7; H, 4·4; N, 6·2; P, 13·6%). The solid is stable in air, but a sample (0·68 g., 0·001 mole), dissolved in hot ethanol in air, produced a transient green colour, and evaporation of solvent gave a sticky solid. Extraction with chloroform (20 ml.) gave cyanuric acid (0·11 g., 93·5%), having m. p. >320° (sublimation) after recrystallisation from water. The filtrate was concentrated to *ca.* 5 ml.; addition of light petroleum then gave diphenylphosphinic acid (0·51 g., 80%), m. p. and mixed m. p. 196—198°. The infrared spectrum was identical with that of an authentic sample.

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