Phosphorus–Nitrogen Compounds. Part XLII.[1] Reactions of *PPP*-Triphenylphosphazene with Organic Acid Halides and Mononuclear Phosphorus Halides

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PPP-Triphenylphosphazene, $Ph_3P{=}NH$ (tpp), reacts with simple acyl halides in benzene to afford excellent yields of *N*-acylmonophosphazenes and aminotriphenylphosphonium halide. Triphenylphosphazenyl-*sym*-triazines can also be prepared but no more than two Ph_3PN moieties can be introduced by this route. The ease of replacement of halogen by triphenylphosphazenyl is very dependent on the nature of the other groups present in the halide substrate, the Ph_3PN group exerting a much more powerful retarding effect than most other substituents. Thiophosphorus(v) halides react similarly to chloro-*sym*-triazines and the same substituent effect is noted. With phosphorus(III) halides, only one triphenylphosphazenyl group has been introduced by this route. Chloramination of diphenyl(triphenpyphosphazenyl)phosphine affords a hydrolytically stable diphosphazenium chloride, which may be converted into a previously reported phosphazenium bromide which had been incorrectly assigned a triphosphazenium structure.

N-ACYL-*PPP*-TRIPHENYLPHOSPHAZENES can be regarded either as *N*-phosphoranylideneamides or as *N*-acylphosphinimides. Accordingly, the synthetic approaches to these compounds have involved either initial generation of a $\equiv C{-}N{=}$ bond, followed by formation of the $-N{=}P\equiv$ linkage, or the reverse.

The first compound of this type was reported by Staudinger,[2] who obtained from the pyrolysis of a 1 : 1 mixture of benzoyl azide and triphenylphosphine a high yield of *N*-benzoyl-*PPP*-triphenylphosphazene, $Ph_3P{=}NCOPh$. The reaction has been widely applied to other systems [3-6] and a comprehensive compilation of physical data and original literature sources is to be found in a recent review by Singh and Zimmer.[7] From the wide spectrum of compounds to which this reaction has been applied, the overall reaction stoicheiometry can be written as in equation (1).

$$\mathrm{RCON_3 + PPh_3 \xrightarrow{Heat} RCON{=}PPh_3 + N_2} \qquad (1)$$

Instead of using an azide as starting material, Kirsanov developed a novel synthesis utilising certain amino-derivatives. Following early work on the condensation of aromatic amines with phosphorus pentachloride, it was found that the same type of reaction occurred with equal facility with acylamides.[8] The general form of the Kirsanov reaction [8] is in equation (2)

$$\mathrm{ZNH_2 + PCl_5 \xrightarrow{Heat} ZN{=}PCl_3 + 2HCl} \qquad (2)$$

where Z = aryl, RCO, RSO_2, *etc.* The *N*-acyl-*PPP*-trichlorophosphazenes generated in this reaction may be quickly and cleanly arylated by organometallic reagents, essentially without any by-products,[8] as in equation (3). In certain acyl systems, the intermediate

$$\mathrm{RCON{=}PCl_3 + 3MgBrPh \longrightarrow RCON{=}PPh_3 + 3\ MgBrCl} \qquad (3)$$

N-acyl-*PPP*-trihalogenophosphazene may be dispensed with and the $-N{=}PPh_3$ group formed directly by substituting dichloro- or dibromo-triphenylphosphorane [9] for PCl_5. This approach has been applied with success to chlorocyclophosphazenes [10] and *sym*-triazines.[11,12]

Acylamides provide a starting point for a third method of synthesis. If an amide is halogenated at nitrogen, the resulting *N*-halogenoamide reacts readily with PPh_3, in the presence of a halogen scavenger to form an acylmonophosphazene. The route is particularly applicable to oxidatively unstable volatile phosphines since reaction occurs at fairly low temperatures. Normally, copper powder is used as the halogen scavenger [equation (4)].[13,14]

$$\mathrm{RCONCl_2 + PPh_3 \xrightarrow[Heat]{Cu} RCON{=}PPh_3 + Cu_2Cl_2} \qquad (4)$$

Each of the above preparative routes is based on the final generation of a phosphazenyl group, and essentially requires at least two stages from an acyl halide. For this reason it has become obvious that more attractive syntheses may be achieved by commencing with a reactive nucleophilic monophosphazene and then acylating this with appropriate reagents.

The simplest approach is *via* *PPP*-triphenylphosphazene, $Ph_3P{=}NH$ (tpp). This monophosphazene, first isolated by Appel *et al.*[15] is a strong base and a strong nucleophile and readily reacts with acyl halides to form *N*-acylphosphazenes, although to date there are relatively few reports pertaining to this type of synthesis.[15-17]

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Usually, 2 mol of monophosphazene are required for each halogen atom to be replaced, since for each 1 mol of a base is consumed as hydrogen-halide scavenger [equation (5)]. In the course of our present studies we have

$$\mathrm{RCOCl} + 2\mathrm{Ph_3P{=}NH} \longrightarrow \mathrm{RCON{=}PPh_3} + [\mathrm{Ph_3PNH_2}]\mathrm{Cl} \quad (5)$$

investigated the preparation of selected *N*-acyl-*PPP*-triphenylphosphazenes with a view to confirming the scope of reaction (5), prepared some triphenylphosphazenyl-*sym*-triazines, and examined briefly the feasibility of employing this procedure in the stepwise synthesis of acyclic arylphosphazenes.

RESULTS AND DISCUSSION

Benzoyl chloride reacted exothermically at room temperature in dry benzene with 2 mol of tpp to afford a quantitative yield of insoluble aminotriphenylphosphonium chloride and, on evaporation of the benzene filtrate, a 90% yield of *N*-benzoyl-*PPP*-triphenylphosphazene, $\mathrm{Ph_3P{=}NCOPh}$, m.p. 193 °C. Essentially the same results were obtained with acetyl, toluene-*p*-sulphonyl, and 4-nitrobenzoyl chlorides. Freshly sublimed cyanogen bromide similarly reacted with tpp in benzene to give the theoretical yield of aminotriphenylphosphonium bromide and *ca.* 85% of the expected *N*-cyano-*PPP*-triphenylphosphazene, $\mathrm{Ph_3P{=}N{-}C{\equiv}N}$,[16] m.p. 196 °C. Because of the low solubility of the *N*-cyanomonophosphazene in benzene, it is necessary to extract the precipitated aminophosphonium salt several times with hot benzene, which probably accounts for our yield being much higher than that reported by Kirsanov and his co-workers.[16]

1,3,5-Trichlorotriazine, ' cyanuric chloride ' ($\mathrm{C_3N_3Cl_3}$), has three ' acyl ' chlorines. Treatment of this compound in dry benzene with 2 mol of tpp affords an almost quantitative yield of the triphenylphosphazenyl-*sym*-triazine, $\mathrm{C_3N_3Cl_2(NPPh_3)}$, (I), m.p. 210 °C. A second halogen is only displaced with great difficulty, requiring the use of chloroform as solvent at 100 °C for 48 h. By this method the bis(triphenylphosphazenyl) derivative, $\mathrm{C_3N_3Cl(NPPh_3)_2}$, (II), m.p. 226—229 °C, was formed in 65% yield. Compound (II) did not react further with tpp under any of the conditions investigated. Similarly, dichlorodimethylamino-*sym*-triazine, $\mathrm{C_3N_3Cl_2(NMe_2)}$, reacted slowly with tpp in boiling benzene to form the asymmetric chloro(dimethylamino)(triphenylphosphazenyl)-*sym*-triazine, $\mathrm{C_3N_3Cl(NMe_2)(NPPh_3)}$, (III), m.p. 224 °C, in high yield. Attempts to replace the last chlorine atom by tpp were unsuccessful.

Complete replacement of all three chlorine atoms of a *sym*-triazine ring by $\mathrm{Ph_3PN}$ groups is obviously very difficult, if not impossible. The introduction of such groups into a *sym*-triazine deactivates other electrophilic centres to nucleophilic attack. Such an effect has already been clearly illustrated from our work on cyclophosphazenes.[18] In the ground state the electron supply of a $\mathrm{Ph_3PN}$ group is of the order of a primary or secondary alkylamino-group. This has been demonstrated by *X*-ray crystallographic [19,20] and ^{35}Cl n.q.r. spectroscopic data.[18,21] Auxochromic shifts in the u.v. spectra of suitable chromophoric compounds yield similar information.[22] As 1,3,5-trichlorotriazines and hexachlorocyclotriphosphazatrienes can be fully aminolysed by aliphatic amines, steric factors must obviously play an important part when $\mathrm{Ph_3P{=}NH}$ is a reagent and/or a substituent.

The asymmetric compound (III) showed a temperature-dependent ^{1}H n.m.r. spectrum with a coalescence temperature of *ca.* 40 °C for the methyl proton signals. Hexamethylmelamine, $\mathrm{C_3N_3(NMe_2)_3}$, is known to have a planar heavy-atom framework in the solid state.[23] This, together with the short exocyclic C–N bond distances, suggests a considerable amount of π character in these bonds. Triphenylphosphazenylcyclophosphazenes show also short exocyclic P–N bonds.[19] In addition this substituent can adopt different conformations with respect to the ring.[20] Hence further discussion of this phenomenon must await a determination of the energy barrier involved and/or an *X*-ray structure analysis.

Previous approaches to phosphazenyl-*sym*-triazines have utilised either the azide route [6] or the Kirsanov reaction with melamine [12] or partially aminated fluoro-*sym*-triazines. The latter approach was very suitable for the synthesis of tris(triphenylphosphazenyl)-*sym*-triazine, $\mathrm{C_3N_3(NPPh_3)_3}$,[12] since the Kirsanov reaction will be favoured by increased nucleophilicity in the triazine substrate imparted by the presence of $\mathrm{Ph_3PN}$ groups. As might be anticipated, the $\mathrm{C_3N_3(NPPh_3)_3}$ was not isolated as the free base but as a hydrochloride adduct.

Phosphorus(V) halides react equally well (compared with the above organic acid halides) with tpp and similar criteria apply to the replacement pattern. Thus, diphenylphosphinothioic chloride, $\mathrm{Ph_2P(S)Cl}$, reacted exothermically at room temperature with the monophosphazene in dry benzene to afford the triphenylphosphazenyl derivative, $\mathrm{Ph_3P{=}N{-}PPh_2(S)}$, (IV), m.p. 174 °C, in good yield. Phenylphosphonothioic dichloride, $\mathrm{PhP(S)Cl_2}$, having two replaceable halogens, presents somewhat greater difficulty, the first halogen being much more easily replaced than the second. At room temperature, one chlorine was readily replaced by a $\mathrm{Ph_3PN}$ group on treatment with tpp in benzene since the theoretical yield of aminophosphonium chloride was isolated. The presence of $\mathrm{Ph_3P{=}N{-}PPhCl(S)}$ was indicated by the isolation of its

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dimethylamino-derivative when the filtrate of the above reaction was treated with an excess of dimethylamine. The derivative, (dimethylamino)-phenyl(triphenylphosphazenyl)phosphine sulphide, $Ph_3P=N-PPh(NMe_2)(S)$, (V), m.p. 175 °C, was isolated in over 50% yield, a good indication of the relative difficulty of replacing the second chlorine atom of the precursor halide with a $Ph_3P=N-$ group. A benzene solution of phenyl(triphenylphosphazenyl)phosphinothioic chloride, $Ph_3P=N-PPhCl(S)$, did not react with tpp in benzene at room temperature. However, when the reagents were heated in benzene under reflux for 10 h complete replacement occurred, yielding the expected bis(triphenylphosphazenyl) derivative, $(Ph_3P=N)_2PPh(S)$, (VI), m.p. 200 °C. These three P^V compounds are crystalline solids which are quite stable in air.

When the P^V compounds are replaced by the rather more basic P^{III} derivatives the reaction pattern is somewhat modified. Thus chlorodiphenylphosphine, PPh_2Cl, reacted exothermically with tpp in benzene to form the expected phosphazenylphosphine, $Ph_3P=N-PPh_2$, (VII), m.p. 125 °C, previously isolated by Nöth and his co-workers [24] and aminotriphenylphosphonium chloride. Compound (VII) is a strong nucleophile and reacted exothermically with sulphur in benzene to form the sulphide (IV) and with gaseous chloramine to form pentaphenyldiphosphazenium chloride, $[Ph_3P=N-PPh_2-NH_2]Cl$, (VIII), m.p. 246 °C.

The phosphazenium salt (VIII) is ionic and can be readily converted into the bromide form by the use of an anion-exchange resin in methanol. The resulting pentaphenyldiphosphazenium bromide, $[Ph_3P=N-PPh_2-NH_2]Br$, (IX), m.p. 233 °C, is identical in every respect to an acyclic phosphazenium bromide reported by us some years ago and at that time tentatively (and erroneously) assigned the structure of a heptaphenyltriphosphazenium bromide.[25] Since the C, H, and N analyses for the two phosphazenium salts are similar (Calc. for $Ph_7N_3P_3H\cdot HBr$: C, 66.6; H, 4.90; N, 5.55. Calc. for $Ph_5N_2P_2H\cdot HBr$: C, 64.8; H, 4.85; N, 5.00%) there is little doubt that the original assignment was due to a poor analysis. The present assignment is, however, unambiguous since the complete analyses for the chloride and bromide derivatives are in excellent agreement with calculated values and also, of course, from the method of synthesis.

Attempts to replace the two chlorines of dichlorophenylphosphine by tpp did not, however, proceed analogously. Reaction in benzene between an excess of tpp and the halide afforded a heavy white precipitate which did not react with chloramine and which contained all the reaction products, the only product in solution being unchanged tpp. It is probable that the initial product formed is a strong base and is precipitated as a hydrogen chloride adduct, together with tpp·HCl. A quarternisation reaction has also been observed by Schmidbaur and his co-workers in the reaction of PMe_2Cl with the silylated trimethylphosphazene, $Me_3P=N-SiMe_3$.[26]

From these results it is seen that the major limitations on the use of ' free ' monophosphazenes are first that the phosphazenyl substituent itself reduces the electrophilicity of other acyl-halogen groups to such an extent that further substitution is strongly retarded, and secondly that the basicity of the product should be less than tpp itself. For the latter reason, polysubstitution by tpp and other alkyl- and aryl-monophosphazenes is probably carried out more easily *via* the silazyl derivative, as first used by Nöth and his co-workers,[24] for in this case no free acid is generated during the reaction. However, where low degrees of substitution are required, the mildness, specificity, and cleaness of the free tpp reaction has many advantages over other methods, particularly in sensitive systems.

We summarise the advantages and disadvantages of the various methods of introducing phosphazenyl groups into molecules as follows. (*i*) Free phosphazenes are considerably more reactive than their silylated analogues. The latter are, however, hydrolytically more stable, give volatile by-products, and use only 1 mol of reagent per group introduced. (*ii*) Both the free phosphazenes and their silylated analogues suffer pronounced retardation (from a combination of steric and polar effects) as more and more phosphazenyl groups are introduced into a given molecule. (*iii*) The azide method is potentially hazardous, but in it, as in (4) the Kirsanov reaction (where hydrolytically unstable reagents are involved), the reaction sites in polyfunctional substrates are further removed from each other, hence less interaction takes place and larger numbers of phosphazenyl groups can be introduced into a given molecule (*cf. sym*-triazines).

EXPERIMENTAL

Benzene and light petroleum (b.p. 60—80 °C) were distilled from sodium hydride and stored over granular alumina. Chloroform was dried by prolonged contact with granular alumina. All liquid acyl halides were degassed *in vacuo* to remove hydrogen halides and then distilled either at low pressure or under nitrogen, after which they were used immediately. Cyanogen bromide was sublimed at atmospheric pressure under nitrogen and trichloro-*sym*-triazine (cyanuric chloride) was recrystallised from light petroleum and stored in a desiccator over sodium hydroxide pellets. Dichlorodimethylamino-*sym*-triazine was prepared according to standard methods and recrystallised from benzene–light petroleum (1 : 3) to constant m.p. 148 °C. Gaseous chloramine was prepared according to the method described by Sisler.[27]

Molecular weights were determined on a ' Mechrolab ' vapour-pressure osmometer, using 1,2-dichloroethane as solvent.

Preparations.—N-*Acylmonophosphazenes.* A solution containing *PPP*-triphenylphosphazene (tpp) (0.01 mol, 2.77

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[27] H. Sisler, *Inorg. Synth.*, 1957, **5**, 92.

g) in benzene (50 cm^3) was added with shaking to a solution of acyl halide (0.005 mol) in benzene (100 cm^3). The mixture was allowed to stand at room temperature until no more precipitation occurred and aminotriphenylphosphonium chloride formed as a dense crystalline precipitate. The mixture was then boiled under reflux for *ca.* 5 min and the aminophosphonium salt filtered off on a No. 3 sintered crucible and washed with a little hot benzene. The filtrate and washings were evaporated to dryness under reduced pressure and the residue crystallised from the minimum volume of toluene–light petroleum (1 : 3). In the case of polyhalogen derivatives, the weights of substrate halide and tpp were modified according to the needs of each experiment, as were the conditions. The experimental data are in the Table.

Products of reaction of various halides with *PPP*-triphenylphosphazene (tpp) in benzene

Halide (amount/mol)	Amount of tpp (mol)	$t(\theta_c/°C)$	Product (yield/%)	M.p.,[a] $\theta_c/°C$	Analysis[b]/% C	H	N	P	M[b]
PhCOCl (0.005)	0.01	10 min (25)	$Ph_3P{=}NCOPh$ (90)	193 (192) [8]					
MeCOCl (0.005)	0.01	10 min (25)	$Ph_3P{=}NCOMe$ (91)	177 (164) [13]					
p-$O_2NC_6H_4COCl$ (0.005)	0.01	10 min (25)	$Ph_3P{=}NCOC_6H_4NO_2$ (95)	187	70.3	4.5	6.7		430
					(70.5)	(4.5)	(6.6)		(426)
$p$$MeC_6H_4SO_2Cl$ (0.005)	0.01	10 min (25)	$Ph_3P{=}NSO_2C_6H_4Me$ (93)	195 (193) [5]					
$N{\equiv}C{-}Br$ (0.01)	0.02	10 min (25)	$Ph_3P{=}NCN$ (85)	196 (194) [16]					
$C_3N_3Cl_3$ (0.01)	0.02	1 h (25)	$C_3N_3Cl_2(NPPh_3)$ (95)	210	59.0	3.5	13.1		415
					(59.3)	(3.5)	(13.4)		(425)
$C_3N_3Cl_2(NPPh_3)$ (0.01)	0.02[c]	2 d (100)	$C_3N_3Cl(NPPh_3)_2$ (65)	226—229	70.1	4.5	10.4		660
					(69.8)	(4.5)	(10.5)		(665.5)
$C_3N_3Cl_2(NMe_2)$ (0.01)	0.02	1 h (81)	$C_3N_3Cl(NMe_2)(NPPh_3)$ (80)	224	63.6	4.8	16.0		440
					(63.6)	(4.85)	(16.2)		(433.5)
$Ph_2P(S)Cl$ (0.005)	0.01	10 min (25)	$Ph_3P{=}NPPh_2(S)$ (75)	174 (174) [4]	72.8	5.2	3.0		500
					(73.0)	(5.0)	(2.8)		(493)
$PhP(S)Cl_2$ (0.005)	0.02	10 h (81)	$(Ph_3P{=}N)_2PPh(S)$ (50)	200	73.0	5.0	4.2		675
					(72.8)	(5.1)	(4.0)		(692)
PPh_2Cl (0.02) [d]	0.04	10 min (25)	$Ph_3P{=}NPPh_2$ (65)	125 (124) [24]	77.0	5.4		13.2	
					(78.0)	(5.4)		(13.1)	

[a] Literature values are given in parentheses. [b] Calculated values are given in parentheses. [c] In chloroform. [d] Reaction and crystallisation were carried out entirely under dry nitrogen.

(Dimethylamino)phenyl(triphenylphosphazenyl)phosphine sulphide, (V). To phenylphosphonothioic dichloride (0.01 mol, 2.1 g) in benzene (20 cm^3) was added with shaking a solution of tpp (0.02 mol, 5.5 g) in benzene (50 cm^3). The mixture was stirred under nitrogen for 20 min, after which the mixture was heated to boiling for 10 min, allowed to cool, and finally filtered under nitrogen. Dimethylamine (0.04 mol, 1.8 g) was added to the filtrate and the mixture heated under reflux for 3 h. After filtering off the precipitated amine hydrochloride, the filtrate was evaporated to dryness and the residue recrystallised from toluene–light petroleum to give (dimethylamino)phenyl(triphenylphosphazenyl)phosphine sulphide, (V) (2.5 g, 55%), m.p. 175 °C (Found: C, 67.5; H, 5.5; N, 5.9%; *M* 450. $C_{26}H_{26}N_2P_2S$ requires C, 67.8; H, 5.65; N, 6.1%; *M* 460).

Pentaphenyldiphosphazenium chloride, (VIII), *and bromide*, (IX). A chloramine–ammonia mixture was passed through a solution of diphenyl(triphenylphosphazenyl)-phosphine, (VII) (0.01 mol, 4.6 g), in benzene (150 cm^3) at room temperature for 30 min. The precipitate was filtered off, dried *in vacuo*, and recrystallised from acetone to give (VIII) (3.5 g, 68%), m.p. 246 °C (Found: C, 69.9; H, 5.3; P, 12.2. $C_{30}H_{27}ClN_2P_2$ requires C, 70.2; H, 5.3; P, 12.1%). The solution of the salt in methanol gave an immediate precipitate of silver(I) chloride on treatment with alcoholic silver(I) nitrate.

A solution of (VIII) (0.005 mol, 2.6 g) in methanol (10 cm^3) was eluted with methanol through a short column containing ion-exchange resin (20 mmol) in the bromide form. The eluate was evaporated to dryness on a rotary evaporator at 40 °C and the residue recrystallised from acetone to give (IX) (1.6 g, 57%), m.p. 233 °C (Found: C, 65.1; H, 5.0; P, 11.3. $C_{30}H_{27}BrN_2P_2$ requires C, 64.8; H, 4.9; P, 11.2%). The i.r. spectrum was identical with that of the earlier reported ' heptaphenyltriphosphazenium salt ',[25] as was the m.p. Furthermore, there was no melting-point depression in mixtures of the two substances.

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