Mixed Arsenic–Phosphorus–Nitrogen Heterocycles: Preparation of Derivatives of $1,3,5,2\lambda^5,6\lambda^5,4\lambda^5$-Triaza-arsatriphosphorine

By **D. Bryan Sowerby** * and **R. Jonathan Tillott**, Department of Chemistry, University of Nottingham, Nottingham NG7 2RD

Ring-closure reactions occur when the linear phosphazene $[(NH_2)Ph_2PNPPh_2(NH_2)]Cl$ and substituted arsenic(V) chlorides react leading to products containing a new heterocyclic system based on N_3P_2As rings. A hydrochloride salt, $N_3(PPh_2)_2AsPh_2{\cdot}HCl$, has been isolated in which protonation occurs at a ring nitrogen atom, most probably that adjacent to the arsenic atom. Chloride attached to arsenic in the N_3P_2As system is readily replaced by methoxy- or dimethylamino-groups.

COMPOUNDS containing the formally unsaturated cyclotriphosphazene ring system (N_3P_3) are well known, as are compounds containing larger phosphorus–nitrogen rings. Examples of compounds containing the analogous arsenic–nitrogen systems are much rarer, but the phenyl derivatives, $N_3As_3Ph_6$ [1] and $N_4As_4Ph_8$,[2] have been characterized by *X*-ray methods and preparative details are available for $(NAsMe_2)_3$,[1] $(NAsRCl)_n$,[3] and $[NAs(OR)_2]_n$.[4]

A number of systems in which one or two phosphorus atoms of the N_3P_3 system are replaced by a second non-metal atom have also been described but the formal unsaturation is maintained only in those systems involving carbon or sulphur, *i.e.* C_2N_3P,[5] CN_3P_2,[6] S_2N_3P,[7] and SN_3P_2.[8] In these cases, incorporation of a hetero-atom from the first row of the Periodic Table or one with an extra electron is likely to modify greatly the bonding in the ring system. To obviate these effects it was of

---

[1] L. K. Krannich, U. Thewalt, W. J. Cook, S. R. Jain, and H. H. Sisler, *Inorg. Chem.*, 1973, **12**, 2304.

[2] M. J. Begley, D. B. Sowerby, and R. J. Tillott, *J.C.S. Dalton*, 1974, 2527.

[3] V. Krieg and J. Weidlein, *Angew. Chem. Internat. Edn.*, 1971, **10**, 516; H. J. Vetter, H. Nöth, and W. Jahn, *Z. anorg. Chem.*, 1964, **328**, 144.

[4] H. Preiss and D. Hass, *Z. anorg. Chem.*, 1974, **404**, 190.

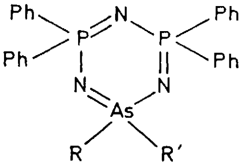
[5] A. Schmidpeter and C. Weingand, *Angew. Chem. Internat. Edn.* 1971, **10**, 396.

[6] A. Schmidpeter and J. Ebeling, *Chem. Ber.*, 1968, **101**, 3883.

[7] H. H. Baalman and H. C. van der Grampel, *Rec. Trav. chim.*, 1973, **92**, 712; R. Clipsham and M. A. Whitehead, *J.C.S. Faraday II*, 1972, 72.

[8] H. H. Baalman and H. C. van der Grampel, *Rec. Trav. chim.*, 1973, **92**, 1237.

interest to attempt the preparation of arsenic-substituted phosphazenes as here the major influences on ring bonding would arise from the increased atomic radius of arsenic (*ca.* 1.21 Å compared with 1.10 Å for phosphorus) and the lower π-bonding potential of arsenic due to diffuseness of the 4*d* orbitals. The well known linear phosphazene, $[(NH_2)Ph_2PNPPh_2(NH_2)]Cl$, which contains an N_3P_2 chain, was the starting material for the synthesis.



	R	R′
(1)	Ph	Ph
(2)	Ph	Cl
(3)	Me	Me
(4)	Ph	OMe
(5)	Ph	NMe_2

EXPERIMENTAL

Chlorodiphenylphosphine, prepared by redistribution of dichlorophenylphosphine in the presence of aluminium trichloride,[9] was chlorinated in dichloromethane solution at −78 °C to give PPh_2Cl_3. Iminobis(aminodiphenylphosphine) chloride, $[(NH_2)Ph_2PNPPh_2(NH_2)]Cl$, was then obtained from ammonia and PPh_2Cl_3 by the method of Schmulbach and Derderian.[10] Diphenylarsenic trichloride and phenylarsenic tetrachloride were obtained by the low temperature (−78 °C) chlorination of respectively chlorodiphenylarsine and dichlorophenylarsine which were themselves isolated as products from the redistribution of mixtures of triphenylarsine and arsenic trichloride.[11] Chlorodimethylarsine,[12] obtained by reducing dimethylarsinic acid, was chlorinated at −78 °C in dichloromethane to give the corresponding trichloride.

All the solvents were dried by conventional methods and reactions were carried out under anhydrous conditions in an atmosphere of nitrogen.

Preparations.— 2,2,4,4,6,6-*Hexaphenyl*-1,3,5,2λ⁵,6λ⁵,4λ⁵-*triaza-arsatriphosphorine*, $N_3(PPh_2)_2AsPh_2$ (1). Diphenylarsenic trichloride (1.6 g, 4.9 mmol) in dichloromethane (50 cm³) was added dropwise to a solution of $[(NH_2)Ph_2PNPPh_2(NH_2)]Cl$ (2.2 g, 4.9 mmol) in dichloromethane (50 cm³) at room temperature. A solution of triethylamine (3 cm³) in dichloromethane (20 cm³) was then added and the mixture was stirred for 1 h. After removal of the solvent, the residue was extracted with hot toluene to leave as an insoluble residue the expected quantity of triethylamine hydrochloride. Concentration of the toluene solution gave colourless *crystals* (2.7 g, 85% yield) which after recrystallization from acetonitrile melted at 207—208 °C (Found: C, 66.7; H, 4.5; N, 6.8. Calc. for $C_{36}H_{30}AsN_3P_2$: C, 67.4; H, 4.7; N, 6.6%).

$N_3(PPh_2)_2AsPh_2\cdot HCl$. Diphenylarsenic trichloride (3.5 g, 10.4 mmol) and $[(NH_2)Ph_2PNPPh_2(NH_2)]Cl$ (4.5 g, 10.0 mmol) were heated under reflux in toluene (150 cm³) until hydrogen chloride evolution ceased (18 h). After filtration, the yellow solution was concentrated to yield colourless *crystals*, m.p. 167—168 °C (2.0 g, 29%) (Found: C, 63.8; H, 4.8; Cl, 5.5; N, 6.4. Calc. for $C_{36}H_{31}AsClN_3P_2$: C, 63.8; H, 4.6; Cl, 5.2; N, 4.6%).

$N_3(PPh_2)_2AsPhCl$ (2). A solution of phenylarsenic tetrachloride (7.6 g, 25.7 mmol) in dichloromethane (70 cm³) was added dropwise to $[(NH_2)Ph_2PNPPh_2(NH_2)]Cl$ (11.6 g, 25.7 mmol) in the same solvent (80 cm³). Triethylamine (30 cm³) in dichloromethane (30 cm³) was added and the mixture was stirred at room temperature for 2 h. The expected amount of triethylamine hydrochloride was filtered off and the filtrate was evaporated to dryness. The remaining white *solid*, (2), was recrystallized from toluene, m.p. 135—136 °C (Found: C, 60.3; H, 4.0; N, 7.2. Calc. for $C_{30}H_{25}AsClN_2P_2$: C, 60.0; H, 4.2; N, 7.0%).

$N_3(PPh_2)_2AsMe_2$ (3). The method was similar to that described for compound (2) above, yield 55%, m.p. 174—175 °C (Found: C, 59.6; H, 5.3; N, 8.0. Calc. for $C_{26}H_{26}AsN_3P_2$: C, 60.2; H, 5.1; N, 8.1%).

Reactions of (2) *with* Na(OMe) *and* NMe_2H.—A solution of sodium methoxide in methanol was added dropwise to compound (2) also in methanol solution. After stirring for 1 h the methanol solution was decanted from the precipitated sodium chloride and evaporated to dryness. The solid remaining was recrystallized from toluene (60% yield) to give pure $N_3(PPh_2)_2AsPh(OMe)$ (4), m.p. 195 °C (Found: C, 61.8; H, 4.7; N, 6.7. Calc. for $C_{31}H_{28}AsN_3OP_2$: C, 62.5; H, 4.7; N, 7.1%).

Anhydrous dimethylamine was passed into a solution of (2) in diethyl ether held at 0 °C until no further precipitation of dimethylamine hydrochloride occurred. After filtration and evaporation of the solvent, the residue was recrystallized from toluene to give pure $N_3(PPh_2)_2AsPh(NMe_2)$ (5) (53%), m.p. 138 °C (Found: C, 62.5; H, 4.9; N, 9.0. Calc. for $C_{32}H_{31}AsN_4P_2$: C, 63.1; H, 5.1; N, 9.2%).

DISCUSSION

Compounds (1)—(3) containing the previously unknown N_3P_2As heterocyclic system resulted readily by the loss of hydrogen chloride from substituted arsenic(V) chlorides and the linear phosphazene, iminobis(aminodiphenylphosphine) chloride, but triethylamine was necessary for complete removal of hydrogen chloride. Reactions carried out without a tertiary base led to a monohydrochloride salt as product. Most reactions were carried out at room temperature in order to minimize dissociation and/or reorganization of the arsenic(V) chloride; this is particularly important with $AsPhCl_4$ and $AsMe_2Cl_3$.

The single chlorine atom in (2) was replaced on reaction with sodium methoxide or anhydrous dimethylamine giving (4) and (5) respectively, but attempts to prepare the fluoride using $K[SO_2F]$ or a thiocyanate from ammonium thiocyanate were not successful and only unidentified ring-cleavage products were isolated. The monochloride (2) reacts quickly with moisture in the atmosphere and there is mass-spectrometric evidence for an oxygen-bridged species, $O[N_3(PPh_2)_2AsPh]_2$, from a peak at *m/e* 1 144.

N.M.R. Spectra.—The ¹H n.m.r. spectrum of (1) showed complex multiplets centred at τ *ca.* 2.20 and *ca.* 2.70 in the ratio 2 : 3, corresponding respectively to the *o*- and *m*- plus *p*-hydrogens. The signal for the former was shifted downfield due to the deshielding

---

[9] M. P. Brown and H. B. Silver, *Chem. and Ind.*, 1961, 24.

[10] C. D. Schmulbach and C. Derderian, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1395.

[11] A. G. Evans and E. Warhurst, *Trans. Faraday Soc.*, 1948, **44**, 189.

[12] G. P. van der Kelen, *Bull. Soc. chim. belges*, 1956, **65**, 343.

effect of the ring. An alternative explanation, *i.e.* that the two multiplets arise from signals due to phenyl groups attached to arsenic and phosphorus respectively, seems to be ruled out as there is little difference between the chemical shifts of aromatic protons for other phenylphosphorus and -arsenic compounds.[13] The methyl protons of compounds (3)—(5) all showed a singlet but, in agreement with the strong deshielding effect of the ring, the signal for (3) (τ 7.82) was shifted downfield from that for trimethylarsine[14] (τ 9.06) while for (4) and (5) the signals (τ 6.57 and 7.54, respectively) are close to those for the analogous arsenic(III) compounds.[14]

Protonation of a ring nitrogen in the hydrochloride of (1) seems likely from the occurrence of an n.m.r. peak corresponding to a single proton at τ −1.57 in agreement with data for other comparable protonated heterocycles.[6,15] There is some ambiguity, however, about the protonation site, but on the basis of relative electronegativities the formation of a P–$\overset{+}{\mathrm{N}}$H–As group rather than P–$\overset{+}{\mathrm{N}}$H–P is likely.

Infrared Spectra.—All the compounds gave complex i.r. spectra with, as expected, many bands in common. Two aspects of the vibrational behaviour are however of interest; first the identification of bands associated with the phenyl groups attached to phosphorus and arsenic, and secondly the assignment of absorptions due to vibrations of the N_3P_2As ring.

The absence of specific bands which can be correlated with the stretching and deformation modes of Ph–M bonds has been discussed extensively[16] and it is clear that mixing occurs with the mass-sensitive phenyl modes designated[17] as *q*, *r*, *y*, and *t*. Selected i.r. bands for the compounds are given in the Table which also includes suggested assignments. Except for (3), bands due to phenyl groups attached to both phosphorus and arsenic are found in the 1 080—1 130, 660—720, 460—540, and 320—440 cm^{-1} regions, with the phosphorus components occurring at higher energy. In some cases it is possible to assign the asymmetric and symmetric modes expected for a MPh_2 group; for example in the spectrum of (2), the bands at 1 120 and 1 095 cm^{-1} are the two components of *q* due to the PPh_2 group, while the single band at 1 080 cm^{-1} is associated with the single phenyl group attached to arsenic. There is a similar situation for the *y* mode with two components at 544 and 527 cm^{-1} for phosphorus and one at 472 cm^{-1} for the arsenic atom.

Infrared data

Compound					
(1)	(2)	(3)	(4)	(5)	Proposed assignment
1 195s	1 185s	1 180s	1 185s	1 187s	Ring stretch and *a* *
1 180s					
1 166s	1 169s		1 176s	1 168s	Ring stretch and *c*
1 119s	1 120s	1 127s	1 115s	1 118s	*q* (P)
1 100s	1 095s	1 105s	1 095s		
1 090s	1 080s		1 088s	1 090s	*q* (As)
1 067ms	1 066s	1 073m	1 064s	1 066s	*d*
1 024ms	1 027s	1 030s	1 017s	1 020s	Ring stretch and *b*
	1 018s				
755mw	780s	760m	757m	760m	Ring elongation
720m	720s	721s	718s	718s	*r*(P)
670w	670mw		667ms	670m	*r* (As)
590m	590ms	586s	580ms	585mw	Ring deformation
542s	544s	540s	541s	543s	*y* (P)
530ms				530s	
525m	527s	526s	523s	524s	
480w	472m		472mw	474mw	*y* (As)
463w					
435w	435mw	430w	434m	435mw	*t* (P)
334w	329mw		322mw	320w	*t* (As)

* For meaning see ref. 17.

Vibrational spectra of trimeric phosphazenes are generally interpreted on the assumption of a planar ring system with D_{3h} symmetry, but in the arsenic compound (1) the highest symmetry will lead to the point C_{2v}. This means that 11 i.r.-active ring modes, divided into ring stretches ($3A_1 + 3B_2$), in-plane deformations ($2A_1 + B_2$), and out-of-plane deformations ($2B_1$), will be expected compared with four modes for the N_3P_3 or N_3As_3 systems. The other compounds will belong to the C_s point group and 12 i.r.-active ring modes are expected. A general examination of the i.r. listings points to a number of bands common to all the five compounds which are not associated with vibrations of phenyl or other exocyclic groups. For example, there are two strong bands between 1 170 and 1 190 cm^{-1} and one at *ca.* 1 020 cm^{-1} corresponding loosely to the degenerate ring-stretching modes observed at *ca.* 1 200 and *ca.* 950 cm^{-1} in the spectra of trimeric phosphazenes and arsazenes respectively. The band at *ca.* 760 cm^{-1} has counterparts at *ca.* 900 (N_3P_3) and *ca.* 630 cm^{-1} (N_3As_3) and can be assigned as a ring-elongation mode, while the peak at *ca.* 580 cm^{-1} is probably the analogue of the in-plane deformation assigned at *ca.* 650 cm^{-1} in trimeric phosphazenes.

---

[13] H. H. Sisler and S. R. Jain, *Inorg. Chem.*, 1968, **7**, 104.

[14] M. Durand and J. P. Laurent, *Bull. Soc. chim. France*, 1973, 2169.

[15] M. Bermann and K. Utvary, *J. Inorg. Nuclear Chem.*, 1969, **31**, 271.

[16] K. M. Mackay, D. B. Sowerby, and W. C. Young, *Spectrochim. Acta*, 1968, **24A**, 611.

[17] D. H. Whiffen, *J. Chem. Soc.*, 1956, 1350.

The hydrochloride salt of (1) gave an i.r. spectrum similar to that of (1), except that (*a*) two weak broad bands were found at 2 680 and 2 230 cm^{-1} [ν(NH)] in agreement with protonation having occurred at a ring nitrogen atom, (*b*) the high-energy ring-stretching modes were raised to 1 220 and 1 175 cm^{-1}, and (*c*) a new band appeared at 910 cm^{-1}. The major bonding consequence of protonation will be to restrict the full development of a π_s system in the heterocycle, although both σ and π_a bonding will also be affected due to decreased electronegativity of the protonated nitrogen atom. The increase in energy of the ring modes, however, implies a greater localization of π bonding in the N_2P_2 segment while the band at 910 cm^{-1} can be associated with a more localized As=N bond.

One of us (R. J. T.) thanks the S.R.C. for a Research Studentship.

[6/1379 *Received*, 14*th July*, 1976]