Diazaphosphetidinones with Four-co-ordinated Phosphorus †

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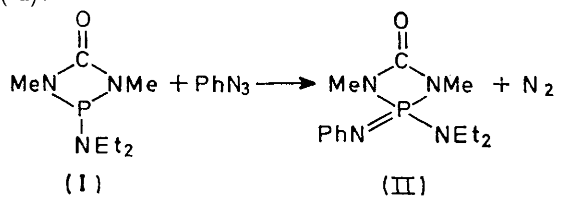
Three new compounds based on the P–N–C(O)–N ring have been prepared and are described. They exhibit the following structures: $(Et_2N)(Ph)$P–NMe–C(O)–NMe, NP$(Ph)_2$–NP$(Ph)_2$–NP–NMe–C(O)–NMe, and [Me-N–C(O)–NMe–P(O)–$]_2$O. These compounds are the first examples of diazaphosphetidinones based on four-co-ordinated phosphorus.

ALTHOUGH several diazaphosphetidinones exhibiting the endocyclic sequence P–N–C(O)–N are known,[1] no such compounds containing a four-co-ordinated phosphorus atom have been reported.[2] A previous attempt to obtain such a compound from a ring closure of phenyliminodialkylaminophosphorus(V) dichlorides, $PhN{=}P(NR_2)Cl_2$ ($R = Et$ or Bu^n), with *N,N'*-disubstituted ureas $(R'NH)_2CO$ ($R' =$ Me or Ph) resulted[3] in the hydrolysis of the former compounds to give pyrophosphates $[PhNHP(NR_2)(O)]_2O$. Here, synthesis of diazaphosphetidinones exhibiting a four-co-ordinated phosphorus atom has been attempted through three theoretically possible routes: (*a*) oxidation of a diazaphosph(III)etidinone, (*b*) reaction of a diazaphosph(V)etidinone based on five-co-ordinated phosphorus to form a diazaphosph(V)etidinone with four-co-ordinated phosphorus, and (*c*) reactions of substrates with four-co-ordinated phosphorus.

RESULTS AND DISCUSSION

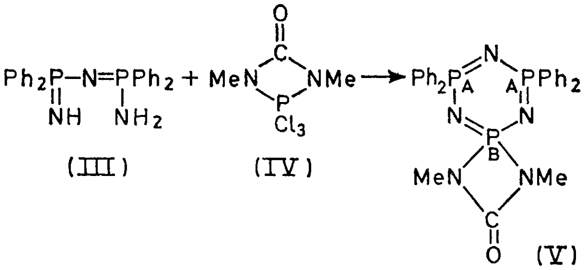
(a) *Oxidation of a Diazaphosph*(III)*etidinone*.—No defined products were obtained by an attempted oxidation of 2-diethylamino-1,3-dimethyl-1,3-diaza-2-phosph(III)etidin-4-one (I), with oxygen, sulphur, or trimethylborane. However, oxidation with phenyl azide gives, in a smooth reaction, 2-phenylimino-2-diethylamino-1,3-dimethyl-1,3-diaza-2-phosph(V)etidin-4-one (II):



(1)

The formation of (II) is shown by the oxidation of the phosphorus atom as monitored by ^{31}P n.m.r. [δ_P −87·8 p.p.m. for (I) and δ_P − 11·6 p.p.m. for (II)]. Although the ^1H n.m.r. spectrum exhibits higher-order splitting, the peak areas and the effect of phosphorus decoupling are in accord with the assigned structure. The strong band at 1260—1240 cm^{-1} in the i.r. spectrum is characteristic for the phosphimido-function (⋝P=N–) and further confirms the structure.

(b) *Reactions of a Diazaphosph*(V)*etidinone*.—The reaction of (III) with (IV) yields (V), which may be named



(2)

1,3-dimethyl-6,6,8,8-tetraphenyl-1,3,5,7,9-penta-aza-4,6,8-triphosphaspiro[3.5]nona-4,6,8-trien-2-one. This latter compound contains a phosphorus atom of a diazaphosph(V)etidinone exhibiting four nearest neighbours. Structural evidence given by the ^{31}P n.m.r. spectrum indicates two different kinds of phosphorus atoms, P_A and P_B, to be present in the ratio $P_A : P_B = 2 : 1$; the chemical shifts and coupling constants are in accord with the proposed structure. Compound (V) represents one of the very few known spirocyclic P–N molecules having unequal ring sizes.[4]

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[1] For a comprehensive review, see M. Bermann, in *Adv. Inorg. Chem. Radiochem.*, 1972, **14**, 1.

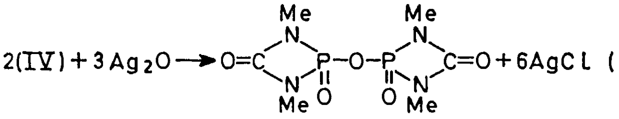
[2] A related compound has been reported by M. V. Kolotilo and G. I. Derkach, *Zhur. obshchei. Khim.*, 1969, **39**, 463 (*Chem. Abs.*, 1969, **70**, 115261).

[3] M. Bermann and K. Utvary, *Synth. Inorg. Metalorg. Chem.*, 1971, **1**, 171.

[4] See T. Chivers and R. Hedgeland, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 767; *Canad. J. Chem.*, 1972, **50**, 1017.

Attempts to convert the $\gt PCl_3$ group of (IV) to a $\gt P(O)Cl$ group by reaction with either sulphur dioxide or acetic anhydride failed.

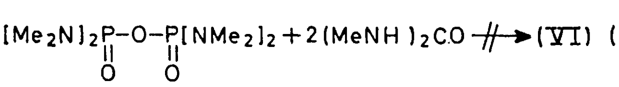
Another diazaphosphetidinone exhibiting a four-co-ordinated phosphorus atom is obtained as a substituted pyrophosphoric acid derivative in very low yields, equations (3) and (4). No reaction between *N*,*N*′-dimethylurea and octamethylpyrophosphorylamide, OMPA, (transamination) occurred [see equation (5)].



(3)

(VI)

$$2(MeNH)_2CO + P_2O_3Cl_4 \longrightarrow (VI) + 4HCl \qquad (4)$$



$$[Me_2N]_2P(O){-}O{-}P(O)[NMe_2]_2 + 2(MeNH)_2CO \not\longrightarrow (VI) \qquad (5)$$

The structure of compound (VI) is proven by the sharp doublet of the methyl groups (J_{PNCH_3} 8 Hz) in the ^1H n.m.r. spectrum; the ^{31}P n.m.r. spectrum shows the theoretical septet, which collapses into a sharp singlet upon decoupling all the hydrogens. In the i.r. spectrum of (VI), $\nu_{P=O}$ is found at 1350—1300 cm^{-1} and the vibration for the P–O–P linkage may be assigned[5] to the strong bands at 910 cm^{-1} (ν_{as}) and 690 cm^{-1} (ν_s); the carbonyl stretching frequency is found at 1710 cm^{-1}.

(c) *Specific Ring-closure Reaction.*—In a previous attempt,[3] ring closure of *N*,*N*′-disubstituted ureas with phenyliminodialkylaminophosphorus(V) dichlorides resulted in the formation of pyrophosphates (*i.e.* the urea acted only as a water donor). In this study, the reactive hydrogens of the urea were substituted by trimethylsilyl-groups but the desired reaction did not take place:

$$[PhN{=}PNEt_2]Cl_2 + [Me_3SiNMe]_2CO \not\longrightarrow (II) \qquad (6)$$

Since Si–N cleavages are readily achieved with phosphorus fluorides, an attempt to prepare $PhN{=}P[NPh_2]F_2$ was made; but diethylaminotetrafluorophosphorane was obtained[6] upon fluorination (using either SbF_3 or AsF_3) of $PhN{=}P[NEt_2]Cl_2$.* Thus, diazaphosphetidinones exhibiting four-co-ordinated phosphorus were not obtained by the specific ring-closure reactions investigated.

EXPERIMENTAL

Materials.—All solvents used were 'spectrograde' quality and practically water free. *N*,*N*′-Dimethylurea (Eastman) was dried for several hours *in vacuo* at elevated temperature; sulphur dioxide (Matheson) was dried by passage over P_4O_{10}; and octamethylphosphoramide (OMPA) (K & K) was purified by careful fractionation. The following starting materials were prepared according to literature methods: phenyliminodiethylaminophosphorus(V) dichloride,[7] *N*,*N*′-dimethyl-*N*,*N*′-bis(trimethylsilyl)urea,[8] diethylaminodichlorophosphine,[9] phenyl azide,[10] 2,2,2-trichloro-1,3-dimethyl-1,3-diaza-2-phosphetidin-4-one (IV),[11] silver oxide,[12] and diphosphoric acid tetrachloride (pyrophosphoryl chloride), $P_2O_3Cl_4$.[13] Iminobis(aminodiphenylphosphonium) chloride[14] was converted to the free phosphinimine (III), with a freshly prepared sodium methoxide solution.[15] All materials agreed in their physical properties with published data, except for the ^1H n.m.r. spectrum of (IV) in which we found, in accordance with a recent report,[16] no evidence for a geometrical isomerism;[11] the ^1H n.m.r. spectrum (neat liquid) consists of a doublet at τ 7·27 (J_{CH_3NP} 21·0 Hz) and the ^{31}P n.m.r. spectrum exhibits the theoretical septet at $\delta_P = +59{\cdot}4$ p.p.m. (J_{PNCH_3} 20·9 p.p.m.). This compound, (IV), reacts very violently with water, explosively for several grams in running water.

Analyses and Spectra.—Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz. M.p.s were obtained on a Mel-Temp m.p. block and are uncorrected. I.r. spectra were recorded either as films in the case of liquids or as KBr pellets (0·5%) for solid substances, using a Beckman IR-10 spectrometer. ^1H N.m.r. spectra were obtained in $CDCl_3$ solutions on a Varian A-60 spectrometer, using TMS as an internal standard. The ^{31}P n.m.r. spectra were carried out with a Varian XL-100-15 spectrometer, operating at a frequency of 40·55 MHz and locked onto the deuterium resonance of D_2O. The samples were contained in 5 mm o.d. tubes which were concentrically inserted, using Teflon spacers, into a thin-wall 12 mm o.d. tube containing the D_2O. Where desirable, the phosphorus spectrum was decoupled from all the protons. The i.r. data are given in Supplementary Publication No. 20637 (2 pp.).†

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* No fluorination occurred with NaF–acetonitrile; however, a mixture of Et_2NPF_4 and $PhN{=}P[NEt_2]F_2$ (as evidenced by ^1H n.m.r.) was obtained by fluorination with Na_2SiF_6, but it could not be separated by distillation.

† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. supplied as full size copies).

[5] See D. E. C. Corbridge in 'Topics in Phosphorus Chemistry,' eds. M. Grayson and E. J. Griffith, Interscience, New York, vol. 6, p. 235 ff., 1969.

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[8] J. F. Klebe, J. B. Bush, jun., and J. E. Lyons, *J. Amer. Chem. Soc.*, 1964, **86**, 4400; J. F. Klebe, F.P. 1434770/1966 (Compagnie Francaise Thomson-Houston) *Chem. Abs.*, 1966, **65**, 20163; U.S.P. 3346609/1967 (General Electric Co.) B.P. 1106523/1968; G.P. 1518935/1969.

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[14] I. I. Bezman and J. H. Smalley, *Chem. Ind.* (*London*), 1960, 839; U.S.P. 3080422/1963 (Armstrong Cork Co.) *Chem. Abs.*, 1963, **59**, 8790; I. I. Bezman, U.S.P. 3098871/1963 (Armstrong Cork Co.); *Chem. Abs.*, 1963, **59**, 14024; R. G. Rice and B. Grushkin, U.S.P. 3329716/1967 (W. R. Grace & Co.); G.P. 1222500/1966; B.P. 1016467/1966; *Chem. Abs.*, 1966, **64**, 17639.

[15] A. Schmidpeter and J. Ebeling, *Angew. Chem.*, 1967, **79**, 534; *Angew. Chem. Internat. Edn.*, 1967, **6**, 565; *Chem. Ber.*, 1968, **101**, 2602.

[16] R. E. Dunmur and R. Schmutzler, *J. Chem. Soc.* (*A*), 1971, 1289.

Preparation of 2-*Diethylamino*-1,3-*dimethyl*-1,3-*diaza*-2-*phosph*(III)*etidin*-4-*one* (I).—This compound was prepared in the same way as similar diazaphosph(III)etidinones.[17]

Under a blanket of nitrogen, a solution of Et_2NPCl_2 (90·0 g) in tetrahydrofuran (50 ml) was added slowly to an intensely stirred solution of *N,N'*-dimethylurea (45·5 g) in tetrahydrofuran (600 ml) containing triethylamine (116·5 g). The system was kept at a temperature of 0—5° with a NaCl–ice bath. A precipitate was formed immediately. Stirring was continued for 3 h and the triethylamine hydrochloride (96·4% of theory) filtered off in a dry box; the solvent was removed from the filtrate by means of a rotary evaporator (temperature not to exceed 30°) leaving a slightly yellow oil. Distillation at 86·5°, 0·55 Torr afforded the colourless product (I) (55·2 g, 56·5% of theory) (Found: C, 44·75; H, 8·25; N, 22·1; P, 16·7. $C_7H_{16}N_3OP$ requires C, 44·45; H, 8·55; N, 22·2; P, 16·35%).

^{1}H N.m.r. spectrum: $\tau_{CH_2} = 6{\cdot}95$ (d, q), τ_{CH_3} (ring) $= 7{\cdot}23$ (d), τ_{CH_3} (ethyl group) $= 8{\cdot}90$ (t), $J_{CH_3CH_2}$ 7·3 Hz, J_{CH_2NP} 9·2 Hz, J_{CH_3NP} 8·0 Hz. Phosphorus spectrum: $\delta_P = -87{\cdot}8$ p.p.m. (neat).

Preparation of 2-*Phenylimino*-2-*diethylamino*-1,3-*dimethyl*-1,3-*diaza*-2-*phosphetidin*-4-*one* (II).—Under nitrogen, a solution of phenyl azide (7·78 g) in benzene (20 ml) was added slowly to a stirred solution of (I) (12·35 g) in benzene (40 ml), and nitrogen was evolved in a slightly exothermic reaction. The system was maintained at 30—40° with a water bath. With addition completed, the mixture was stirred for 1 h at room temperature and 1/2 h at 60°. Filtration in the absence of moisture yielded pure white crystals of (II) (15·7 g, 86% of theory), m.p. 111°, slightly hydroscopic (Found: C, 55·4; H, 7·35; N, 19·8; P, 11·3. $C_{13}H_{21}N_4OP$ requires C, 55·7; H, 7·55; N, 20·0; P, 11·05%).

^{1}H N.m.r. spectrum (higher order): $\tau_{C_5H_5}$ (area 5H) $= 2{\cdot}82$, τ_{CH_2} (area 4H) $= 6{\cdot}75$ (q, d), τ_{CH_3} (ring) (area 6H) $= 7{\cdot}25$ (d) and 7·88 (pseudo triplet), τ_{CH_3} (ethyl group) (area 6H) $= 8{\cdot}68$ (multiplet); $J_{CH_3CH_2}$ 7·0 Hz, J_{CH_3NP} 12·0 Hz, J_{CH_3NP} 6·5 Hz. Phosphorus spectrum: $\delta_P = -11{\cdot}6$ p.p.m. ($CHCl_3$).

Other oxidations of (I): No defined products could be obtained by the reaction of (I) with oxygen (air), sulphur, or trimethylborane.

Reaction of (III) *with* (IV).—Under stirring, a suspension of (III) (10·70 g) in toluene (100 ml) and containing triethylamine (12 ml) and (IV) (5·76 g) was heated 4 h under reflux. Filtering the hot mixture gave triethylamine hydrochloride (8·7 g, 87·8% of theory). The solvent was removed from the filtrate, yielding a thick brownish oil; addition of acetonitrile (30 ml) gave, when stood in the refrigerator, white crystals of (V) (8·1 g, 61·5% of theory); m.p. 194—195° (decomp.) (Found: C, 64·1; H, 5·0; N, 8·5; P, 18·6. $C_{27}H_{26}N_3OP_3$ requires C, 64·65; H, 5·25; N, 8·4; P, 18·55%).

^{1}H N.m.r. spectrum: $\tau_{C_6H_5} = 2{\cdot}10, 2{\cdot}30, 2{\cdot}58$ (complex multiplet), $\tau_{CH_3} = 7{\cdot}36$ (d); $J_{P_BCH_3}$ 13·5 Hz. Phosphorus spectrum (proton decoupled) in $CHCl_3$: $\delta_{P_A} = -21{\cdot}1$ p.p.m. (d), $\delta_{P_B} = -11{\cdot}9$ p.p.m. (t), $J_{P_AP_B}$ 13·0 Hz, ratio $P_A : P_B = 2 : 1$ (theor. 2 : 1).

Reaction of (IV) *with Silver Oxide*.—With exclusion of light, finely ground Ag_2O (15·05 g) was suspended in benzene (150 ml) and a solution of (IV) (9·70 g) in benzene (30 ml) was added dropwise over a period of 10 min. Heating under reflux for 4 h, filtration, and stripping of the solvent gave a yellow oil. Acetonitrile was added and the mixture stood in the refrigerator, which then yielded small amounts (0·7 g, 11·4% of theory) of white crystalline (VI); m.p. 288° (Found: C, 25·2; H, 4·2; N, 19·4; P, 21·75. $C_6H_{12}N_4O_5P_2$ requires C, 25·55; H, 4·3; N, 19·9; P, 21·95%).

^{1}H N.m.r. spectrum: $\tau_{CH_3} = 6{\cdot}78$ (d), J_{PNCH_3} 8 Hz. Phosphorus spectrum: $\delta_P = +11{\cdot}0$ p.p.m. (CH_2Cl_2).

Reaction of $P_2O_3Cl_4$ *with* N,N'-*Dimethylurea*.—Some $(MeNH)_2CO$ (6·35 g) was dissolved in benzene (150 ml) containing triethylamine (22 ml) and then a solution of $P_2O_3Cl_4$ (9·08 g) in benzene (30 ml) was added over 5 min (exothermic reaction). Heating under reflux for 3 h and filtering the triethylamine hydrochloride and stripping of the solvent yielded a brownish oil. Addition of acetonitrile allowing the mixture to stand for several days in the refrigerator afforded very small amounts of compound (VI), identical in mixed m.p. and n.m.r. spectra with the compound obtained above.

Caution: This pyrophosphate (VI) should be regarded as highly toxic and as a potential anticholinesterase agent and therefore its solutions should be handled with greatest care.

Attempted Reactions.—No reaction was observed between OMPA and *N,N'*-dimethylurea in boiling benzene (10 h). Further, there was no reaction of (IV) with acetic acid anhydride in boiling benzene; the products were recovered unchanged. When excess SO_2 was bubbled into a benzene solution of (IV) for 1 h and the solvent evaporated, ^{31}P n.m.r. gave evidence of ring opening; but we were unable to define the products (sometimes an oil and sometimes a waxy solid). In the attempted reaction of phenyliminodiethylaminophosphorus(V) dichloride with *N,N'*-dimethyl-*N,N'*-bis(trimethylsilyl)urea, equimolar amounts of $PhN{=}PNEt_2Cl_2$ (4·40 g) and $[Me_3SiNMe]_2CO$ (3·88 g) in bromobenzene (30 ml) were refluxed under a blanket of nitrogen for 20 h. Fractionation was found to give only the starting materials.

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