## Organophosphorus Intermediates. Part IV.<sup>1</sup> Formation of Phenylphosphinidene in the Decomposition of Phenylphosphinic Anhydride: Mechanism for the Thermal Decomposition of Monosubstituted Phosphinic Acids

By M. J. Gallagher\* and I. D. Jenkins, School of Chemistry, University of New South Wales, Kensington, N.S.W., 2033 Australia

Phenylphosphinidene, formed in the decomposition of phenylphosphinic anhydride, has been trapped by reaction with benzil to give a spirophosphole (4).

Phenylphosphinic acid and pentaphenylcyclopentaphosphine react readily by an ionic mechanism to give phenylphosphine and phenylphosphonic anhydride. The two reactions provide an explanation of the thermal decomposition of monosubstituted phosphinic acids to give phosphines and phosphonic acids.

Phosphorous and hypophosphorous acid also react with pentaphenylcyclopentaphosphine to give phosphine and phenylphosphine together with a complex mixture of other products.

Free-radical abstraction of hydrogen from phenylphosphinic acid converts it into pentaphenylcyclopentaphosphine and polymeric phenylphosphonic anhydride. Phenylphosphine is similarly converted into the polyphosphine in good yield.

A COMMON feature of the chemistry of the lower oxyacids of phosphorus is their thermal degradation to give phosphines, a process loosely described as disproportionation.<sup>2</sup> Decomposition of phosphonic (phosphorous) acid in this way is the basis of a laboratory preparation of phosphine itself:<sup>3</sup>

$$4HP(:O)(OH)_2 \longrightarrow PH_3 + 3H_3PO_4 \qquad (1)$$

and until relatively recently an analogous reaction was the basis for the most general method of preparing primary phosphines: 4

$$3RPH(:O) \cdot OH \longrightarrow RPH_2 + 2RP(:O)(OH)_2$$
 (2)

Hypophosphorous (phosphinic) acid undergoes thermal decomposition to give, among other products, phosphine and phosphorus.<sup>2</sup> Nothing is known concerning the mechanisms of any of these reactions and they have been little studied. Kosolapoff found that primary phosphinic acids were trimeric in solution and suggested that similar aggregates might be involved in the decomposition of these compounds to primary phosphines.<sup>5</sup> We have previously reported <sup>6</sup> that phenylphosphinic anhydride decomposed at room temperature into a mixture of phenylphosphonic acid, phenylphosphine, and pentaphenylcyclopentaphosphine and suggested that the anhydride might be involved in the thermal decomposition of the parent acid. Here, we describe further experiments designed to test this hypothesis.

We originally suggested <sup>6</sup> that phenylphosphinic anhydride, (1), broke down to phenylphosphinic acid and phenylphosphinidene, and the latter either abstracted hydrogen to give phenylphosphine, (2), or polymerized to the cyclic polyphosphine (3).

Attempts to trap the phosphinidene with diethyl

disulphide<sup>6,7</sup> gave ambiguous results but we now find that decomposition of the anhydride in the presence of a

large excess of benzil gives rise to the phosphole (4).<sup>7</sup> The yield of the adduct was low (ca. 1%) but larger quantities of benzoin (12%) the expected hydrolysis product of the spirophosphole (4), were also obtained. The reaction was carried out in the dark and at room temperature and under these conditions neither of the phosphines (2) or (3) gives any detectable amount of this heterocycle. This constitutes very strong evidence for the formation of phenylphosphinidene in the decomposition of the anhydride (1).



In addition to the reaction with diethyl disulphide, a number of other potential traps were examined without success. In boiling toluene a barely detectable (by g.l.c.) amount of dibenzyl was formed. With azobenzene in hot ethyl acetate a rapid reaction occurred affording very insoluble, high melting, apparently polymeric products. Similar behaviour was observed when the polyphosphine (3) was heated with a solution of azobenzene. Tetraphenylcyclopentadienone gave no iddentifiable products.

If all the phosphinidene formed in the anhydride decomposition were consumed by hydride abstraction

<sup>5</sup> G. M. Kosolapoff and J. S. Powell, J. Amer. Chem. Soc., 1950, 72, 4291. <sup>6</sup> M. J. Gallagher and I. D. Jenkins, *J. Chem. Soc.* (C), 1966,

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- <sup>7</sup> U. Schmidt, I. Boie, C. Osterroht, R. Schroer, and H. F. Grutzmacher, Chem. Ber., 1968, 101, 1381.

<sup>&</sup>lt;sup>1</sup> Part III, M. J. Gallagher and I. D. Jenkins, J. Chem. Soc.

<sup>(</sup>C), 1971, 210.
<sup>2</sup> J. R. Van Wazer, 'Phosphorus and Its Compounds,' Interscience, New York, 1958, vol. 1.
<sup>3</sup> S. D. Gokhale and W. L. Jolly, *Inorg. Synth.*, 1967, 9, 56.
<sup>4</sup> A. W. Frank, *Chem. Rev.*, 1961, 61, 389.

2PhPH(:O)·OH 
$$\xrightarrow{\text{heat}}$$
 [PhPH(:O)]<sub>2</sub>O + H<sub>2</sub>O  $\longrightarrow$   
PhP: + PhP(:O)(OH)<sub>2</sub>

$$PhP: + PhPH(:O) \cdot OH \longrightarrow PhPH_2 + PhPO_2$$
 (4)

If phenylphosphine is arising by hydride abstraction from phenylphosphinic acid then similar behaviour would be expected with other free-radical sources. Such abstraction does, in fact, occur readily when the acid is boiled in benzene with azobisisobutyronitrile (AIBN). The major products obtained are the polyphosphine (3) and polymeric phenylphosphonic anhydride,  $H(PhPO_2)_nOH$ . The presence of the latter is demonstrated by the formation of morpholinium morpholino(phenyl)phosphinate, (5), when the product mixture is treated with morpholine. The dimeric anhydride affords the salt, (6), under these conditions and this compound is the principal product when the radical abstraction is carried out in the presence of morpholine. No phenylphosphine is expected or found in these reactions as it is converted to the polyphosphine (3) in good yield (70%) by AIBN.

PhPH(:O)·OH 
$$\xrightarrow{\text{AIBN}}_{80^{\circ}}$$
 (PhP)<sub>5</sub> + H(PhPO<sub>2</sub>)<sub>n</sub>·OH  
 $\downarrow$  AIBN, R<sub>2</sub>NH  $\downarrow$  R<sub>2</sub>NH  
PhP(:O)·O·(O:)PPh [R<sub>2</sub>NH<sub>2</sub>]<sup>+</sup> [PhPO] [PhPO] [R\_2NH\_2]^+ [PhPO] [R\_2NH\_2]^+ (PhP)\_5  
(6) 2[R<sub>2</sub>NH<sub>2</sub>]<sup>+</sup> + (PhP)<sub>5</sub>

$$(R_2 H H = \text{horphonice})$$
 Equation (3)  
PhPH<sub>2</sub>  $\xrightarrow{\text{AIBN}}$  (PhP)<sub>5</sub> Equation (6)

Since decomposition of the anhydride (1), normally gives roughly equivalent amounts of the phosphines (2) and (3), unless a large excess of phenylphosphinic acid is present, it seemed unusual that polyphosphines,  $(RP)_n$ , had not been reported as products of thermal decomposition of phosphinic acids if formation of an anhydride was the first step in these reactions. Yields of phosphine as high as 97% based on Eq. 2 may be obtained by modifications of technique.8 One possible explanation was that at the temperatures normally required for thermal decomposition  $(150-200^{\circ})$  the polyphosphine was in equilibrium with the free phosphinidene. Indeed phenylphosphinic acid and the polyphosphine (3) react readily under quite mild conditions (85-90°) giving phenylphosphine and phenylphosphonic anhydride. However, the simple stoicheiometry expected is not observed and an ionic path is followed as shown by the absence of reaction in the presence of an organic base (triethylamine or morpholine). Similarly, no reaction occurs between the polyphosphine, (3), and neutral  $P^{(IV)}$ -H compounds, *e.g.* methyl phenylphosphinate, dimethyl phosphonate, or diphenylphosphine oxide, under conditions where reaction with the acid is complete. In the presence of an acid catalyst, however, the polyphosphine reacts readily with water according to equation (7).

$$(PhP)_{5} + H_{2}O \xrightarrow{H^{+}} PhPH(:O) \cdot OH + PhPH_{2} \quad (7)$$

Finally, when p-tolylphosphinic acid replaces phenylphosphinic acid in this reaction both phenylphosphine and p-tolylphosphine are produced in a 52:48 ratio together with the dimeric anhydride of p-tolylphosphonic anhydride. Hence, although all the anhydride formed arises from the original acid, part of the phosphine arises from the acid also. This is in agreement with the fact that when the proportions of reagents in the polyphosphine-phenylphosphinic acid reaction are varied until complete consumption of both is observed, the stoicheiometry shown in equation (8) is obtained (96% of the phosphorus accounted for), *i.e.* a substantial 3PhPH(:O)·OH + 0·2(PhP).

$$\frac{1.6 \text{PhPH}(\text{:O}) \cdot \text{OH} + 0.2 (\text{PhP})_5}{1.6 \text{PhPH}_2 + 1.13 [\text{PhP}(\text{:O}) \cdot (\text{OH})]_2 \text{O}}$$
(8)

amount of the phenylphosphine arises from the phenyl phosphinic acid. Clearly, the reaction is an ionic one and proceeds in such a fashion as to give rise to an intermediate derived from the acid [very probably the anhydride (1)] which decomposes to the corresponding phosphine.

The source of the hydrogens in the phosphine formed was determined by carrying out the reaction with dideuteriated phenylphosphinic acid, PhPD(:O)OD, prepared by the careful hydrolysis of phenylphosphonous dichloride with deuterium oxide. The close agreement between the deuterium content of this acid (90%) and that of the phenylphosphine produced (85%), precludes any appreciable hydrogen abstraction from other than PH or POH bonds. By careful equilibration of the dideuteriated acid with water, the monodeuterio-acid, PhPD(:O)·OH, was obtained but the deuterium scrambled between the two possible positions under the conditions of the reaction, and precluded the direct determination of whether one or both hydrogen atoms was abstracted. This scrambling is facilitated by gentle warmth or dissolution in a polar solvent (e.g. methanol) though the solid acid is quite stable.

$$PhPCl_{2} + D_{2}O \longrightarrow PhPD(:O) \cdot OD \xrightarrow{H_{2}O} PhPD(:O) \cdot OH \xrightarrow{heat or} PhPH(:O) \cdot OD (9)$$

A possible path for the polyphosphine-phosphinic

 $\ensuremath{^{8}}$  Dr. E. N. Walsh, Stauffer Chemical Co., personal communication.

acid reaction is shown in the Scheme. The stoicheiometry for the sequence shown is close to that observed but this does not, of course, constitute a proof of mechanism; other reasonable paths may be written<sup>9</sup> and the Scheme simply applies Occam's razor.



overall: (PhP)<sub>5</sub>+14 PhPH(:0)·OH

Similarly it should be noted that there is no concrete evidence relating to the mechanism of decomposition of the anhydride (1) and alternatives equally as feasible as our original suggestion <sup>6</sup> may be envisaged.<sup>9,10</sup> Regardless of mechanistic detail, the anhydride decomposition coupled with the acid-catalyzed reaction of the polyphosphine provide a reasonable explanation of the thermal degradation of monosubstituted phosphinic acids. Anhydride formation also rationalizes the ano-

<sup>9</sup> I. D. Jenkins, Ph.D. Thesis, University of New South Wales,

1969. <sup>10</sup> A. J. Kirby and S. G. Warren, 'The Organic Chemistry of Phosphorus,' Elsevier, Amsterdam, 1967. 11

A. Michaelis, Annalen, 1876, 181, 265.

<sup>12</sup> R. S. Davidson, R. A. Sheldon, and S. Trippett, J. Chem. Soc. (C), 1967, 1547.
 <sup>13</sup> R. S. Davidson, R. A. Sheldon, and S. Trippett, J. Chem.

Soc. (C), 1968, 1700.

malous reaction of chlorine with phenylphosphinic acid<sup>11</sup> [equation (10)]. Despite its ready reaction with

$$5PhPH(:O) \cdot OH + 2Cl_2 \longrightarrow PhPH_2 + 4HCl + 2[PhP(:O) \cdot OH]_2O \quad (10)$$

*i.e.* PhPH(:O)·OH + 
$$Cl_2 \longrightarrow$$
  
PhPCl(:O)·OH  $\longrightarrow$  PhPO<sub>2</sub> + HCl  
PhPO<sub>2</sub> + 2PhPH(:O)·OH  $\longrightarrow$   
PhP(:O)(OH)<sub>2</sub> + [PhPH(:O)]<sub>2</sub>O  $\longrightarrow$  etc. (11)

phenylphosphinic acid, the polyphosphine, (3), does not undergo reactions with carboxylic acids or alcohols 12-14 analogous to those observed by Trippett and his coworkers for tetraphenyldiphosphine. Reaction occurs with carbonylic acids but no well defined products are obtained.

The formation of anhydrides in the thermal decomposition of phosphonic and phosphinic acids was first suggested by Joly<sup>15</sup> in 1886. Hossenlop, et al.,<sup>16,17</sup> however, found that the anhydride of phosphonic acid (pyrophosphorous acid) was relatively stable, though attempts to prepare higher anhydrides led to decomposition. A diester of pyrophosphorus acid is sufficiently stable to be distilled,<sup>18</sup> although it decomposes when set aside. This anhydride reacts with amines to give phosphonic amides, though the analogous reaction with phenylphosphinic anhydride leads to rapid decomposition to give phenylphosphinidene.<sup>6</sup> The function of an organic substituent attached directly to phosphorus in producing this marked variation in reaction path is obscure. Also, in our hands the product from the reaction of hypophosphorous acid with dicyclohexylcarbodi-imide does not evolve phosphine at room temperature. Nevertheless, both phosphorous and hypophosphorous acid react with the polyphosphine under conditions (80-90°) in which both acids are stable by themselves. No well defined stoicheiometry was found for either reaction (see Experimental section) but the following equations are representative.

$$\begin{array}{r} \text{HP(:O)(OH)}_{2} + 0.1(\text{PhP})_{5} \longrightarrow \\ 0.5\text{PH}_{3} + 0.02\text{PhPH}_{2} + 0.24\text{H}_{4}\text{P}_{2}\text{O}_{7} + \\ 0.36\text{PhP(O)(OH)}_{2} \quad (12) \end{array}$$

 $\mathrm{H_{2}P(:O)OH} + 0.12(\mathrm{PhP})_{5} \longrightarrow 0.44\mathrm{PH_{3}} +$ 0.12PhPH<sub>2</sub> + (H<sub>4</sub>P<sub>2</sub>O<sub>7</sub> + PhP(O)(OH)<sub>2</sub> + (2 uncharacterized acids) (13)

Little can be said of these reactions except that they are clearly complex in contrast with the phenylphosphinic acid case. Noteworthy is the high yield of phosphine, much higher than obtained in simple pyrolyses.

14 R. S. Davidson, R. A. Sheldon, and S. Trippett, J. Chem. Soc. (C), 1966, 722.

- A. Joly, Compt. Rend., 1886, 102, 760.
   J. P. Ebel and F. Hossenlopp, Bull. Soc. chim. France, 1965, 2219, 2229.
- <sup>17</sup> F. Hossenlop, M. McPartlin, and J. P. Ebel, Bull. Soc. chim. France, 1965, 2221.

<sup>18</sup> A. Zwierzak and A. Koziara, *Tetrahedron*, 1967, 23, 2243.

Although the thermal decomposition of both phosphorous and hypophosphorous acid may proceed *via* anhydrides and phosphinidene intermediates, their full understanding will require detailed study since it is apparent that the fate of the reactive species does not follow the relatively simple path observed for the monosubstituted phosphinic acids.

## EXPERIMENTAL

Instrumentation and general practice were as described previously.<sup>6</sup> All reactions involving tervalent phosphorus compounds were carried out in an atmosphere of dry, commerical, oxygen-free nitrogen. Compounds marked with an asterisk (\*) were identified by direct comparison with authentic samples by at least two independent techniques (m.p., spectra, t.l.c.). Phenylphosphine and pentaphenylcyclopentaphosphine were determined by reaction with tellurium tetrachloride <sup>19</sup> or by gas chromatography (phenylphosphine only). Phosphine itself was identified by its ability to reduce tellurium tetrachloride to the element.

Pentaphenylcyclopentaphosphine. This compound was prepared (75%) from phenylphosphonous dichloride and magnesium turnings in tetrahydrofuran; it was recrystallized from carbon disulphide-ethanol and had m.p. 151—  $153^{\circ}$  (lit.,<sup>20</sup>154—156°). Mass spectra showed the compound to be the pentamer. In several preparations the product was spontaneously inflammable in air. This was attributed to the presence of traces of phenylphosphine and small particle size.

2,3,5,7,8-Pentaphenyl-1,4,6,9-tetraoxa-5-phospha[pv]-

spiro[4,4]nona-2,7-diene.—This compound was prepared by the method of Schmidt, et al.,<sup>7</sup> from magnesium stilbenedioxide and phenylphosphonous dichloride, m.p. 212— 215° (lit.,<sup>7</sup> 216—218°);  $\delta$ <sup>31</sup>P (pyridine), +16.68 ( $\delta$  H<sub>3</sub>PO<sub>4</sub> = 0).

p-Tolylphosphinic Acid.—This compound was prepared by hydrolysis of the corresponding phosphonous dihalide obtained from toluene and phosphorous trichloride by a Friedel–Crafts reaction, m.p. 104–106° (lit.,<sup>21</sup> 104–105°)  $\delta$ : 7.51, (s, 1H, J 567 PH); 2.36 (s, 3H, ArCH<sub>3</sub>), 13.38 [bs, 1H (exch. D<sub>2</sub>O), POH]. The aromatic ring protons appeared as a four proton ABX pattern (A = ortho-H, B = meta-H, X = P)  $\delta$  H<sub>A</sub> 7.65,  $J_{AX}$  13.8;  $\delta$  H<sub>B</sub> 7.23,  $J_{BX}$  3.7;  $J_{AX}$  8.1.

Decomposition of Phenylphosphinic Anhydride in the Presence of Benzil.-Phenylphosphinic acid (2.0 g) in ethyl acetate (8 ml) and benzene (12 ml) was treated with dicyclohexylcarbodi-imide (1.45 g, 0.5 mol) under nitrogen and filtered into an evacuated flask containing benzil (2.95 g, 2 mol). The flask containing the resulting clear yellow solution was stoppered, wrapped in aluminium foil, and set aside at room temperature in the absence of light (ca. 20°, 14 days). Examination of the solution after this time (t.l.c.) revealed the presence of considerable quantities of the phosphole (4). It was recognized by its  $R_{\rm F}$  value (0.65, benzene, silica gel) and its characteristic blue fluorescence when viewed under u.v. light. Benzil ( $R_F 0.5$ ) has a pale green fluorescence. When a solution of the polyphosphine (3) (50 mg) and benzil (200 mg, 4 mol) in benzene (5.5 ml) and ethyl acetate (2 ml) was set aside for the same length of time under the same conditions no trace of the phosphole (4), could be detected. No change occurred when the solution was boiled under nitrogen but when the solution was exposed to light phosphole formation could be detected after 3 weeks. No phosphole could be detected when phenylphosphine replaced the polyphosphine in this experiment.

In a separate experiment with the same quantities as previously, the anhydride was decomposed when boiled for 0.5 h in the absence of light. T.l.c. of the solution was the same as that from the 14-day experiment. The mixture was poured onto a short column of Kieselgel D5 (80 g) under nitrogen and was eluted with dry benzenelight petroleum (2:3). Concentration of the initial fractions and dilution with acetonitrile afforded the crystalline phosphole\* (27 mg, ca. 1%). Further elution of the column afforded benzoin\* (0.25 g). The low yield of the phosphole is certainly due in part to the instability of the substance in solution. Comparative t.l.c. indicated that the actual yield was considerably higher and it is considered that decomposition occurred during isolation.

Phenylphosphinic Acid and Pentaphenylcyclopentaphosphosphine.--The acid (3.0 g) and phosphine (1.14 g, 0.1 mol [*i.e.* 0.5 mol PhP]) were stirred and heated in vacuo (0.1 mmHg) on a water bath  $(85-90^\circ)$  for 2.5 h. Evolved phenylphosphine\* refluxed in the reaction vessel; it was finally distilled into a cold trap  $(-78^\circ)$  and was estimated by gas chromatography (1.5 g, 0.65 mol). The residue was heated under reflux with anhydrous ethyl acetate (20-25 ml) for several hours and was then chilled to deposit dimeric phenylphosphonic anhydride (2.33 g, 0.37 mol), m.p. 115-118°. This compound was identified as follows. (a) Rapid titration with aqueous sodium hydroxide gave an equivalent weight of 153 (C12H12P2O5 requires: 147); (b) treatment of the anhydride (0.2 g) with an excess of morpholine (0.5 ml) in dry ethyl acetate gave the bismorpholinium salt\* of the anhydride (0.298 g, 94%); (c) hydrolysis in boiling, wet ethyl acetate gave phenylphosphonic acid; \* when boiled in methanol it gave a mixture of phenylphosphonic acid and its monomethyl ester (<sup>1</sup>H n.m.r. analysis). Microanalysis agreed with a dihydrate (Found: C, 43.1; H, 5.2; P, 18.5. C<sub>12</sub>H<sub>16</sub>O<sub>7</sub>P<sub>2</sub> requires: C, 43.1; H, 4.8; P, 18.5%).

The same reaction between phenylphosphinic acid and the polyphosphine occurred more slowly in boiling solvents and proceeded at an appreciable rate at room temperature (40% after 10 days in chloroform). However, accurate yields were more difficult to determine under these conditions, and the data collected in Table 1 to show product

TABLE 1  $^a$ 

Reaction of phenylphosphinic acid with pentaphenylcyclopentaphosphine

				%			
				Recovery			
PhPH(:O)·OH	(PhP) <sub>5</sub>	PhPH <sub>2</sub>	(PhP(:O)•OH) <sub>2</sub> O	<sup>▶</sup> of P			
$2 \cdot 0$	$1 \cdot 0$	1.17	0.74	89			
$2 \cdot 0$	$2 \cdot 0$	1.13					
$2 \cdot 0$	0.667	1.07	0.755	96			
$2 \cdot 0$	0.60	1.025	0.75	97			
$2 \cdot 0$	0.8	1.05	0.79	94			
<sup>a</sup> Quantities	are in	mols,	polyphosphine is	considered as			
monomeric. <sup>b</sup> Estimated as morpholinium salt.							

<sup>21</sup> G. M. Kosolapoff, 'Organophosphorus Compounds,' John Wiley, New York, 1950, p. 148.

M. J. Gallagher and I. D. Jenkins, Analyt. Chem., in the press.
 J. J. Daly, J. Chem. Soc., 1964 (Supplement II), 6147.

variation with molar ratios, were carried out in the absence of solvent as described above.

When the reaction was carried out in the presence of bases the polyphosphine\* was recovered in high yield (>90%). Traces of base (<0.1 mol) did not inhibit the reaction.

p-Tolylphenylphosphinic Acid and Pentaphenylcyclopentaphosphine.—The acid (1·2 g) and the polyphosphine (0·25 g, 0·06 mol) were heated together in an evacuated flask (100— 105°, 3 h) and worked up as described above. <sup>1</sup>H n.m.r. analysis of the phosphines (0·46 g) showed the presence of p-tolylphosphine (0·25 mol) and phenylphosphine (0·27 mol). Treatment of the residue with an excess of morpholine in ethyl acetate gave bis-morpholinium p-tolylphosphonic anhydride (1·376 g, 0·36 mol), m.p. 213—217° (ethanol) (Found: C, 53·5; H, 6·3; N, 5·4; P, 12·6.  $C_{22}H_{34}N_2O_7P_2$  requires C, 53·0; H, 6·8; N, 5·6; P, 12·4%);  $\delta$  (D<sub>2</sub>O) 2·31 (s, 6H, ArCH<sub>3</sub>), 3·17, 3·85 (m, 16H, morpholine ring H), 7—7·6 (m, 8H, ArH).

[2H,]Phenylphosphinic acid.—Freshly distilled phenylphosphonous dichloride (10 g) in dry tetrahydrofuran (30 ml) was added dropwise to a boiling solution of deuterium oxide (5 ml) in dry tetrahydrofuran (80 ml) during 2.5 hr. The solution was boiled for a further hour, evaporated to dryness, and the residue was recrystallized (benzene) yielding [<sup>2</sup>H<sub>2</sub>]phenylphosphinic acid (5.78 g, 73%), m.p. 84—87°, v 1750 (PD), 1900—2000 (POD) cm<sup>-1</sup>, <sup>1</sup>H n.m.r. analysis showed the presence of PH (8%) and POH (10%); 8<sup>31</sup>P(CDCl<sub>3</sub>): -19.8 (t[1:1:1], J<sub>PD</sub> 95). Exchange of both deuterium atoms for hydrogen occurred quite rapidly in methanol. Addition of H<sub>2</sub>O to a CDCl<sub>3</sub> solution brought about immediate exchange of POD for POH. If the solution were then dried  $(Na_2SO_4)$  and evaporated at room temperature the monodeuterio-acid was obtained (83% PD by <sup>1</sup>H n.m.r.). When heated (85-90°, 1 h) this acid gave a product containing 39% PD, i.e. equilibration of PD and POH occurred.

 $[^{2}H]$  Phenylphosphinic Acid and Pentaphenylcyclopentaphosphine.—The deuteriated acid (0.3 g) was melted in vacuo with the polyphosphine (0.091 g) at 85—90° (1.5 h) and the  $[^{2}H_{2}]$  phenylphosphine was distilled off. Analysis (<sup>1</sup>H n.m.r.) showed that it was 85% PhPD<sub>2</sub>.

Pentaphenylcyclopentaphosphine and Water.—The polyphosphine (0.5 g) was heated under reflux (10 h) in aqueous 1,2-dimethoxyethane (1:1) under nitrogen in the presence of toluene-*p*-sulphonic acid (0.2 g). All the phosphine had dissolved after 7 h. The excess of solvent and the phenylphosphine\* (0.212 g, 42%) were distilled off and the residue was treated with water and extracted with benzene to isolate phenylphosphinic acid\* (0.21 g, 32%). A similar reaction occurred when phenylphosphinic acid itself was used as catalyst.

The polyphosphine could be heated under reflux in aqueous methanol without change for long periods (70 h), but if dry air was admitted to the reaction vessel the phosphine was slowly converted into methyl phenylphosphinate (i.r. analysis).

Phosphorous Acid and Pentaphenylcyclopentaphosphine.— The crystalline anhydrous acid (1.056 g) and the polyphosphine (1.39 g, 0.2 mol) were melted together (85—90°) and the evolved gas (145 ml, 762 mmHg  $17.5^{\circ} \equiv 0.226$  g,

x

51% PH<sub>a</sub>) was collected over water after a further period of heating (17 h). Gas evolution had ceased after 5 h. Phenylphosphine\* (0.175 g,  $12{\cdot}5\%)$  was pumped off from the residue which on treatment with ethanol gave crude unchanged polyphosphine\* (0.212 g, 15%). Treatment of the filtrate with aqueous barium acetate gave a white powder (1.856 g,  $49\%^*$ ) shown to be the barium salt of phenylphosphonic acid containing a small amount of the dimeric anhydride salt by i.r. spectroscopy and electrophoresis. These figures were fairly reproducible  $(\pm 5\%)$ with regard to the amount of PIII compounds formed but complex reactions are obviously occurring. Thus, if the phenylphosphine was removed as formed and the reaction time shortened (0.75 h) considerably higher yields of this compound were obtained (33%). Numerous experiments (Table 2) invariably yielded complex mixtures of products and no clear cut stoicheiometry. Phosphate appeared to be formed in some reactions but was not identified with certainty. Essentially the same reactions occurred when the reagents were heated in a solvent such as boiling ethyl acetate.

Phosphorous acid itself undergoes no detectable decomposition under these conditions in the absence of the polyphosphine.

TABLE  $2^{a}$ 

Reaction of phosphorous acid with pentaphenylcyclopentaphosphine

Reage	ents b,c			Products (%)	
H <sub>3</sub> PO <sub>3</sub>	(PhP) <sub>5</sub>	$\rm PH_3$	$PhPH_2$	PhP(:O)(OH)2	Pyrophosphate
1(50)	0.8(48)	50	$5 \cdot 0$	43	
1 (74)	0.6(65)	50	$3 \cdot 6$	61	23.5
1(80)	0.45(98)	36	$9 \cdot 4$	89	45.0
a Coi	nditions: 1	eagen	ts melte	d together and	heated (85—90°)

<sup>a</sup> Conditions: reagents melted together and heated (85–90°) till gas evolution ceased. <sup>b</sup> Percentage of reagent accounted for as products and recovered starting material given in parentheses. <sup>e</sup> Expressed in mol; polyphosphine is considered as monomeric.

Hypophosphorous Acid and Pentaphenylcyclopentaphosphine.—Crystalline, anhydrous acid (0.959 g) and polyphosphine (0.945 g, 0.12 mol) were mixed and warmed (70°) but a homogeneous melt did not result; ethyl acetate (5 ml) was added and the solution was kept at 70° (0.5 h) until all the polyphosphine had dissolved; the mixture was then heated under reflux overnight. Gas evolution (142 ml, 20°, 769.3 mmHg  $\equiv 44\%$  PH<sub>3</sub>) was rapid during the initial period of boiling but had virtually ceased after 2 h. Phenylphosphine (0.193 g, 20%) was distilled off and the residue was treated with an excess of aqueous barium acetate to precipitate a mixture of salts (1.341 g). Examination by i.r. and electrophoresis showed the presence of phenylphosphonate and pyrophosphate together with two unidentified anions, one possibly HPO<sub>3</sub><sup>2-</sup>.

A decrease in the phosphine : acid molar ratio to 0.08 gave phosphine (34%) and phenylphosphine (19%) whereas a ratio of 0.16 gave 47 and 16% of these compounds respectively. Hypophosphorous acid itself decomposed only slightly (5%) in boiling ethyl acetate (20 h).

Phenylphosphinic Acid and 2,2'-Azobisisobutyronitrile.— The acid (1.0 g) and the azo-compound (2.36 g, 2 mol) were boiled together in benzene (5 h). Addition of morpholine and further heating (1.25 h) precipitated the bis-morpholinium salt of phenylphosphonic anhydride\* (0.134 g, 8%). Addition of methanol-acetonitrile to the filtrate afforded

<sup>\*</sup> Estimate based on a quantitative determination of the barium (as its sulphate) followed by isolation of phenylphosphonic acid.

pentaphenylcyclopentaphosphine (0.078 g, 11%). Evaporation of the mother liquor and treatment of the residue with ethyl acetate furnished morpholinium morpholino-(phenyl)phosphinate (5), (0.88 g, 40%), m.p. 149—152°.  $\vee$  2650—2240 (<sup>+</sup><sub>H</sub>H<sub>2</sub>), 1200, 1160 (P=O), 950 cm<sup>-1</sup> (PNC) (Found: C, 52.4; H, 7.1; N, 8.3; P, 10.1. C<sub>14</sub>H<sub>23</sub>N<sub>2</sub>O<sub>4</sub>P requires C, 53.4; H, 7.4; N, 8.9; P, 9.8%). This compound is very susceptible to hydrolysis and when boiled briefly in undried solvents it is converted into the anhydride bis-salt in high yield.

From the residue after isolation of the morpholino-(phenyl)phosphinate further quantities of the anhydride bis-salt\* were obtained by recrystallization giving a total yield of 0.310 g (18.6%). Tetramethylsuccinonitrile\* (0.6 g) was also isolated.

When the reaction was repeated in the presence of an excess of morpholine, the anhydride bis-salt\* (64%) and the polyphosphine (10%) were obtained. Reduction in the molar ratio of dinitrile to acid to 1:1 did not affect the

yields appreciably. With only 0.5 mol of dinitrile per mol of acid the yield of phosphine was reduced (5%) but the anhydride bis-salt was unaffected (63%) and phenylphosphine\* (3%) was also isolated. Reduction in the ratio of dinitrile: acid still further resulted in a sharp drop in product formation. No reaction was observed in methanol or ethanol as solvent.

Phenylphosphine and 2,2'-Azobisisobutyronitrile.—The phosphine (1 ml) and the dinitrile (1.5 g, 1 mol) dissolved in benzene (10 ml) were heated under reflux for 9 h. The solution was freeze-dried and the residue was treated with methanol to give pentaphenylcyclopentaphosphine\* (0.7 g, 70%). The only other product identified was tetramethyl-succinonitrile.\*

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