

## Syntheses and Properties of Novel Polyphosphines containing Various Combinations of Primary, Secondary, and Tertiary Phosphorus Atoms †

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Novel polyphosphines can be prepared by the base-catalysed addition of  $R_2P-H$  across the carbon-carbon double bonds of vinylphosphonate esters, followed by reduction with lithium aluminium hydride. Thus a tertiary-primary diphosphine, a tertiary-diprimary triphosphine, a tertiary-triprimary tripod tetraphosphine, and a ditertiary-diprimary linear tetraphosphine have been prepared. Similarly, the tertiary-secondary diphosphine  $Ph_2P \cdot CH_2 \cdot CH_2 \cdot PPh$  can be prepared by base-catalysed addition of diphenylphosphine to isopropyl phenylvinylphosphinate followed by reduction. The secondary-primary diphosphine  $PhPH \cdot CH_2 \cdot CH_2 \cdot PH_2$  can be prepared by the Arbusov reaction of di-isopropoxy(phenyl)phosphine with di-isopropyl 2-bromoethylphosphonate followed by reduction. The i.r.,  $^1H$  n.m.r.,  $^{31}P$  n.m.r., and mass spectra of the new compounds are discussed.

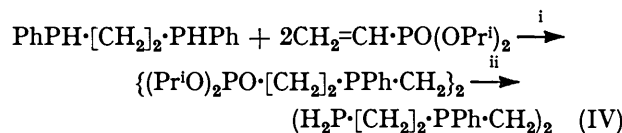
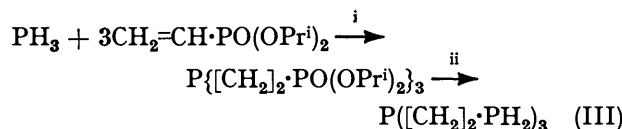
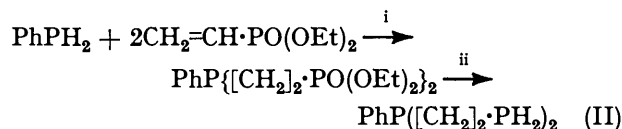
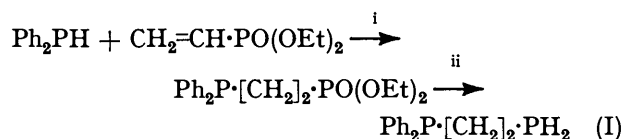
INTEREST in tertiary phosphine complexes of metal halides, carbonyls, and cyclopentadienyls<sup>3-5</sup> led us to develop a new synthesis of potentially polydentate tertiary phosphines<sup>5,6</sup> containing  $P \cdot CH_2 \cdot CH_2 \cdot P$  units by base-catalysed addition of the P-H system across the carbon-carbon double bonds of vinylphosphines. We were also interested in polyphosphines containing the  $P \cdot CH_2 \cdot CH_2 \cdot PH$  and  $P \cdot CH_2 \cdot CH_2 \cdot PH_2$  units for the following reasons. (i) Reactions of such polyphosphines with transition metal derivatives might result in hydrogen loss to give novel metal complexes of polydentate alkyl polyphosphide ligands. (ii) Base-catalysed additions of the P-H systems in these polyphosphines to the vinyl double bonds in vinylphosphorus derivatives should give polytertiary phosphines of more complex structures than those obtained in the previously<sup>5,6</sup> reported syntheses.

### RESULTS

Base-catalysed addition to a vinylphosphonate ester followed by reduction with lithium aluminium hydride of all phosphorus-oxygen bonds was used to convert a P-H bond into a  $P \cdot CH_2 \cdot CH_2 \cdot PH_2$  group. We have used this general synthetic procedure to prepare the tertiary-primary diphosphine (I), the tertiary-diprimary triphosphine (II), the tertiary-triprimary tripod tetraphosphine (III), and the ditertiary-diprimary linear tetraphosphine (IV) according to the illustrated sequences. The intermediate polyphosphorus esters were viscous oils or waxes which could not be readily purified and were not characterized in detail. However, in several cases their  $^1H$  n.m.r. spectra were measured, and exhibited phenyl, alkoxy, and methylene resonances in accord with the proposed structures.

The base-catalysed addition of the P-H system to the carbon-carbon double bond of a dialkyl vinyl-

phosphonate is a special case of Michael addition.<sup>7</sup> Michael additions of diethyl malonate, ethyl acetoacetate, ethyl cyanoacetate, and benzyl cyanide to



i,  $KOBu^t$ -tetrahydrofuran (THF);  
ii,  $LiAlH_4$ - $Et_2O$ [THF for (II)]

diethyl vinylphosphonate have been reported previously.<sup>8</sup> A difficulty in carrying out our addition reactions was the reactivity of the vinylphosphonate ester towards the potassium t-butoxide catalyst in the absence of a P-H compound or other addend. For this reason, the t-butoxide catalyst was not added until after the phosphine and vinylphosphonate had been mixed. In the preparation of the tripod tetraphosphine (III) it was necessary to saturate the mixture of potassium t-butoxide and tetrahydrofuran with phosphine gas before adding the vinylphosphonate ester in order to obtain the desired product (III).

† For a preliminary communication of the preparation of the tertiary-primary diphosphine  $Ph_2P \cdot CH_2 \cdot CH_2 \cdot PH_2$  see ref. 1; for a preliminary communication of some other portions of this work see ref. 2; a portion of this work was presented at the 164th National Meeting of the American Chemical Society, New York, New York, August, 1972, paper INOR 61.

<sup>1</sup> R. B. King and P. N. Kapoor, *Angew. Chem. Internat. Edn.*, 1971, **10**, 734.

<sup>2</sup> R. B. King and J. C. Cloyd, jun., *Z. Naturforsch.*, 1972, **27b**, 1432.

<sup>3</sup> G. Booth, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 1.

<sup>4</sup> T. A. Manuel, *Adv. Organometallic Chem.*, 1965, **3**, 181.

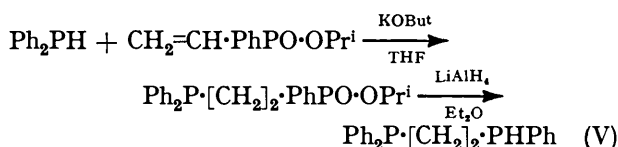
<sup>5</sup> R. B. King, *Accounts Chem. Res.*, 1972, **5**, 177.

<sup>6</sup> R. B. King and P. N. Kapoor, *J. Amer. Chem. Soc.*, 1971, **93**, 4158.

<sup>7</sup> E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. Reactions*, 1959, **10**, 179.

<sup>8</sup> A. N. Pudovik and O. N. Grishina, *Zhur. obshchei Khim.*, 1953, **23**, 267. (*Chem. Abs.*, 1954, **48**, 2573).

A modification of this synthetic principle was used to convert a P-H system into  $P\cdot CH_2\cdot CH_2\cdot PPh$  as follows:



The isopropyl phenylvinylphosphinate was obtained by an Arbusov reaction of di-isopropoxy(phenyl)phosphine with 1,2-dibromoethane followed by dehydrobromination of the resulting 2-bromoethyl derivative with triethylamine.

There are six possible diphosphines with  $CH_2\cdot CH_2$  bridges between the two phosphorus atoms and either hydrogen atoms or phenyl groups in the remaining positions on each phosphorus atom. Of these the ditertiary phosphine  $(\text{Ph}_2\text{P}\cdot\text{CH}_2)_2$ ,<sup>9</sup> the disecundary phosphine  $(\text{PhPH}\cdot\text{CH}_2)_2$ ,<sup>10</sup> and the diprimary phosphine  $(\text{H}_2\text{P}\cdot\text{CH}_2)_2$ <sup>11</sup> have been reported previously. The successful preparations of the diphosphine (V) and the

The  $^1\text{H}$  n.m.r. spectra (Table 1) of the new polyphosphines agreed with the proposed structures. The protons bonded directly to the phosphorus atoms gave the expected widely split doublets ( $J_{\text{PH}}$  ca. 200 Hz) with further triplet fine structure ( $J$  ca. 6–7 Hz) from coupling with a  $CH_2$  group. The secondary phosphine protons showed  $\tau$   $5.89 \pm 0.05$  ( $^1J_{\text{PH}}$   $209 \pm 2$  Hz) whereas the primary phosphine protons showed  $\tau$   $7.29 \pm 0.07$  ( $^1J_{\text{PH}}$   $190 \pm 2$  Hz). The  $P\cdot CH_2\cdot CH_2\cdot P$  protons exhibited broad resonances in the region  $\tau$  7.9–8.6, with  $\text{Ph}_2\text{P}\cdot\text{CH}_2$  at  $\tau$  7.9,  $\text{PhPR}\cdot\text{CH}_2$  ( $R = \text{H}$  or alkyl) at  $\tau$  8.2–8.3, and  $\text{R}_2\text{P}\cdot\text{CH}_2$  ( $R = \text{H}$  or alkyl) at  $\tau$  8.4–8.55.

The  $^{31}\text{P}$  n.m.r. spectra (Table 2) also agreed with the proposed structures. In each case, a  $\text{PH}_2$  group gave a triplet at  $\delta$   $127 \pm 3$  p.p.m. and a secondary PH gave a doublet at  $\delta$   $47 \pm 1$ , with splittings corresponding within experimental error to the corresponding  $^1J_{\text{PH}}$  found from the corresponding proton spectrum (Table 1).

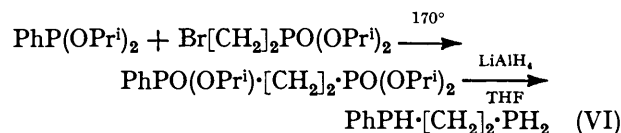
Satisfactory mass spectra of the phosphines (I)–(III) and (VI), were obtained. In each case the molecular ion was observed. Most of the observed fragmentation

TABLE 1  
 $^1\text{H}$  N.m.r. spectra of the polyphosphines

| Compound  | Ph                               | $\tau$ Values ( $J$ in Hz) |   |
|---|----------------------------------|----------------------------|---|
|   |                                  | $CH_2$                     | P-H   |
| $\text{Ph}_2\text{P}\cdot[\text{CH}_2]_2\cdot\text{PPh}^a$                  | 2.78(m)                          | ca. 7.9br(m), ca. 8.2br(m) | 5.84(dt, $J_d$ 208, $J_t$ 6.4)                    |
| $(\text{PhPH}\cdot\text{CH}_2)_2$   | ca. 2.6(m), ca. 2.7(m)           | ca. 8.2(m)                 | 5.88br (d, $J$ 211)                               |
| $\text{Ph}_2\text{P}\cdot[\text{CH}_2]_2\cdot\text{PH}_2$                   | ca. 2.7(m), ca. 2.9(m)           | 7.86(m), 8.52(m)           | 7.23 (dt, $J_d$ 192, $J_t$ ca. 7)                 |
| $\text{PhPH}\cdot[\text{CH}_2]_2\cdot\text{PH}_2$                           | 2.7(m), 2.87(m)                  | ca. 8.2(m), ca. 8.5(m)     | PH: 5.94 (dt, $J_d$ 207, $J_t$ ca. 6.5)           |
| $\text{PhP}([\text{CH}_2]_2\text{PH}_2)_2$                                  | ca. 2.64(m), 2.7(d) ( $J$ ca. 4) | ca. 8.2(m), ca. 8.5(m)     | $\text{PH}_2$ : 7.32 (dt, $J_d$ 191, $J_t$ ca. 7) |
| $\text{P}([\text{CH}_2]_2\text{PH}_2)_2$                                    |                                  | ca. 8.4(m)                 | 7.24 (dt, $J_d$ 188, $J_t$ ca. 7)                 |
| $(\text{H}_2\text{P}\cdot[\text{CH}_2]_2\cdot\text{PPh}\cdot\text{CH}_2)_2$ | 2.68(d), 2.81(d)                 | ca. 8.3(m), ca. 8.55(m)    | 7.22 (d, $J$ 192)                                 |
|   |                                  |                            | 7.35 (dt, $J_d$ 189, $J_t$ ca. 7)                 |

<sup>a</sup>  $\text{CDCl}_3$  solution.

phosphine (I) left only the secondary-primary diphosphine  $\text{PhPH}\cdot[\text{CH}_2]_2\cdot\text{PH}_2$  (VI) to be prepared. An Arbusov reaction of di-isopropyl 2-bromoethylphosphonate with di-isopropoxy(phenyl)phosphine followed by reduction with lithium aluminium hydride was used as indicated:



Again the intermediate phosphorus ester was a viscous liquid which was not purified but was identified from its  $^1\text{H}$  n.m.r. spectrum.

The tertiary-secondary diphosphine (V) was a low-melting crystalline solid which could be purified by low-temperature crystallization from pentane under nitrogen. The remaining new polyphosphines (I)–(IV) and (VI) were colourless, air-sensitive, malodorous liquids, which could be purified by vacuum distillation. The i.r. spectra of all the phosphines (I)–(VI) exhibited a single  $\nu(\text{PH})$  band at  $2286 \pm 1$   $\text{cm}^{-1}$ ; in the case of phosphines containing a  $\text{PH}_2$  group this indicates negligible coupling between the two P-H bonds on the same phosphorus atom.

processes involved rupture of carbon-phosphorus bonds. Elimination of the  $CH_2\cdot CH_2$  bridge from a  $P\cdot CH_2\cdot CH_2\cdot P$  unit was particularly favoured and in some cases

TABLE 2  
 $^{31}\text{P}$  N.m.r. spectra of the polyphosphines <sup>a</sup>

| Compound  | Tertiary |          | Secondary                 | Primary  |                           |
|---|----------|----------|---------------------------|----------|---------------------------|
|   | $\delta$ | $\delta$ | $J_{\text{PH}}/\text{Hz}$ | $\delta$ | $J_{\text{PH}}/\text{Hz}$ |
| $\text{Ph}_2\text{P}\cdot[\text{CH}_2]_2\cdot\text{PPh}^b$                  | +14.1    | +46.6    | 212 $\pm$ 10              |          |                           |
| $(\text{PhPH}\cdot\text{CH}_2)_2$   |          | +47.2    | 211 $\pm$ 5               |          |                           |
| $\text{Ph}_2\text{P}\cdot[\text{CH}_2]_2\cdot\text{PH}_2$                   | +14.7    |          |                           | +124.6   | 191 $\pm$ 10              |
| $\text{PhPH}[\text{CH}_2]_2\cdot\text{PH}_2$                                |          | +48.1    | 208 $\pm$ 10              | +129.1   | 192 $\pm$ 10              |
| $\text{PhP}([\text{CH}_2]_2\text{PH}_2)_2$                                  | +20.7    |          |                           | +126.7   | 191 $\pm$ 10              |
| $\text{P}([\text{CH}_2]_2\text{PH}_2)_2$                                    | +23.0    |          |                           | +125.3   | 191 $\pm$ 10              |
| $(\text{H}_2\text{P}\cdot[\text{CH}_2]_2\cdot\text{PPh}\cdot\text{CH}_2)_2$ | +19.2    |          |                           | +126.7   | 192 $\pm$ 10              |

<sup>a</sup> Resonances to low field of  $\text{H}_3\text{PO}_4$  standard are positive. <sup>b</sup>  $\text{CH}_2\text{Cl}_2$  solution

appropriate metastable ions were observed. Elimination of phosphine was also observed in some of the spectra. In the case of the tetraphosphine (III), phosphine elimination from the ion  $\text{H}_2\text{P}\cdot[\text{CH}_2\cdot\text{CH}_2]_2\text{PH}^+$  was confirmed by a metastable ion at  $m/e$  62.7.

#### EXPERIMENTAL

Microanalyses were performed by Meade Microanalytical Laboratory, Amherst, Massachusetts, and Atlantic Micro-lab, Inc., Atlanta, Georgia. I.r. spectra of liquid

<sup>9</sup> J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1960, 1378.

<sup>10</sup> K. Issleib and H. Weichmann, *Ber.*, 1968, **101**, 2197.

<sup>11</sup> L. Maier, *Helv. Chim. Acta*, 1966, **49**, 842.

compounds were recorded on a Perkin-Elmer 621 spectrometer.  $^1\text{H}$  N.m.r. (Table 1) and  $^{31}\text{P}$  n.m.r. spectra (Table 2) of the liquids were recorded on a Varian HA-100 spectrometer (operating at 100 and 40.5 MHz, respectively). Mass spectra were taken at 70 eV on a Hitachi-Perkin-Elmer RMU-6 spectrometer. The pure liquid polyphosphines were handled in a polyethylene glove bag filled with pure nitrogen. A nitrogen atmosphere was always provided for the following operations: (a) carrying out reactions, (b) handling air-sensitive organophosphorus compounds, (c) admission to evacuated vessels containing potentially air-sensitive materials. In order to minimize exposure of the air-sensitive organophosphorus compounds, a three-necked flask with a fritted disc and stopcock at the bottom was used for filtration of solutions. Because of the offensive odours of most of the organophosphorus compounds used the effluent nitrogen from the reactions was passed through one or more oxidizing traps<sup>6</sup> (*i.e.* calcium hypochlorite, potassium permanganate, bromine water, and/or 1:1 nitric-sulphuric acid) before passing into the fume cupboard exhausts. Aqueous baths of calcium hypochlorite provided an efficient and rapid means of removing odours from glassware exposed to the phosphines.

Potassium *t*-butoxide catalyst (MSA Research Corp., Pittsburgh, Pennsylvania) was often not weighed out but merely added in portions to the mixture of the P-H compound and the vinylphosphonate until the originally colourless mixture became orange or red. This minimized exposure of the *t*-butoxide to the air.

I.r. spectra of the phosphines (I)–(VI) and mass spectra of the phosphines (I)–(IV) and (VI) are reported in Supplementary Publication No. SUP 20795 (5 pp.).\*

**Materials.**—The vinylphosphonate esters were prepared by Arbusov reactions of the corresponding trialkyl phosphites with redistilled 1,2-dibromoethane followed by dehydrobromination of the intermediate 2-bromoethyl derivative with triethylamine in boiling benzene.<sup>12</sup> Other organophosphorus compounds were obtained from the usual commercial sources or prepared as previously described.<sup>6</sup> Tetrahydrofuran was purified by distillation over sodium diphenylketyl under nitrogen.

**Isopropyl Phenylvinylphosphinate.**—1,2-Dibromoethane (*ca.* 450 ml, 4–5 mol) was heated to 140–150° and diisopropoxy(phenyl)phosphine (226 g, 1 mol) was added dropwise. The evolved isopropyl bromide was collected. The mixture was then heated for an additional 2 h. The excess of 1,2-dibromoethane was distilled off at atmospheric pressure (b.p. 131–133°); final traces were removed from the residue at 25° and 0.1 mmHg (several hours). The crude isopropyl 2-bromoethyl(phenyl)phosphinate was boiled under reflux with triethylamine (150 g, 1.5 mol) in benzene (400 ml). The precipitated triethylammonium chloride was filtered off and washed with several portions of benzene. Benzene was removed from the combined filtrate and washings at 25° and 35 mmHg, and the residue was distilled in vacuum to give *isopropyl phenylvinylphosphinate* (147 g, 70%), b.p. 97–100° at 0.1–0.15 mmHg (Found: C, 62.7; H, 7.2.  $\text{C}_{11}\text{H}_{15}\text{O}_2\text{P}$  requires C, 62.8; H, 7.2%),  $\tau$  2.55br, 2.71br and 2.92 (Ph), 3.7–4.9 (complex, vinyl), and 5.88 (sept, *J* 7 Hz) and

9.16 (apparent *t*, separation 7 Hz,  $\text{Pr}^i$ ) (relative intensities *ca.* 5:3:1:6).

**PPP'-Triphenylethylenebisphosphine (V).**—A mixture of diphenylphosphine<sup>13</sup> (37.2 g, 0.2 mol), isopropyl phenylvinylphosphinate (42.0 g, 0.2 mol), and redistilled tetrahydrofuran (300 ml) was treated with solid potassium *t*-butoxide until the mixture became red, with sufficient heat evolution to boil the tetrahydrofuran. The mixture was then boiled under reflux for 16 h. The tetrahydrofuran was removed at *ca.* 25° and 35 mmHg. Attempts to crystallize the residue from propan-2-ol were unsuccessful; it was therefore washed with diethyl ether. The n.m.r. spectrum showed  $\tau(\text{CDCl}_3)$  2.8 (Ph), 2.0 ( $\text{P}\cdot\text{CH}_2$ ), and 5.7 and 8.8 ( $\text{Pr}^i$ ). This adduct (68 g, 0.17 mol) was stirred at room temperature for 4 days with lithium aluminium hydride (20 g, 53 mol) in diethyl ether (*ca.* 400 ml). The mixture was then boiled under reflux for 4 h, cooled (ice-bath), and hydrolysed by successive addition of deoxygenated water (20 ml), aqueous sodium 15% hydroxide (20 ml), and water (60 ml). The ethereal solution was filtered under nitrogen and solvent was removed at 25° and 35 mmHg. The liquid residue was treated with pentane (*ca.* 50 ml) and the resulting solution was cooled to –10°. The precipitate was filtered under nitrogen in a jacketed (–10°) filter and then dried at 25° and 0.1 mmHg to give the *diphosphine* (V) (31 g, 57%), m.p. *ca.* 30° (Found: C, 74.3; H, 6.1; P, 19.3.  $\text{C}_{20}\text{H}_{20}\text{P}_2$  requires C, 74.5; H, 6.2; P, 19.2%).

**PP-Diphenylethylenebisphosphine (I).**—A mixture of diethyl vinylphosphonate (30 g, 0.183 mol), diphenylphosphine<sup>13</sup> (34 g, 0.183 mol), and redistilled tetrahydrofuran (100 ml) was treated with potassium *t*-butoxide (1 g). After the exothermic reaction had subsided, the mixture was boiled under reflux for 20 h. Tetrahydrofuran was removed at *ca.* 25° and 35 mmHg, and the excess of reactants and the other volatile materials were then removed at 85–140° and 0.8 mmHg. The waxy solid residue was refluxed overnight with lithium aluminium hydride (13 g, 0.34 mol) in diethyl ether (*ca.* 200 ml). Hydrolysis with aqueous 6*N*-hydrochloric acid followed by distillation of the dried ( $\text{Na}_2\text{SO}_4$ ) ether layer gave the *diphosphine* (I) (9.6 g, 21%) as a liquid, b.p. 151–152° at 0.5 mmHg [Found: C, 67.6; H, 6.2; P, 23.5%; *M*, 244 (osmometer; in benzene), 246 (mass spec.).  $\text{C}_{14}\text{H}_{16}\text{P}_2$  requires C, 68.3; H, 6.5; P, 25.2%; *M*, 246].

**P-Phenylethylenebisphosphine (VI).**—A mixture of diisopropyl 2-bromoethylphosphonate (41.0 g, 0.15 mol) and diisopropoxy(phenyl)phosphine<sup>14</sup> (33.9 g, 0.15 mol) was heated to 170° in a flask equipped with a distillation head for removal of the isopropyl bromide. Heating was continued until no more isopropyl bromide distilled off. Volatile materials were then removed by vacuum distillation up to 70° at *ca.* 0.5 mmHg. Diisopropyl vinylphosphonate (*ca.* 8 g, 28%) was collected and identified by comparison of its  $^1\text{H}$  n.m.r. spectrum with that of an authentic sample. The residue (46 g) exhibited the expected Ph,  $\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{P}$ , and  $\text{Pr}^i$  resonances in the  $^1\text{H}$  n.m.r. spectrum.

This crude product (45 g) was boiled under reflux for 5 h with lithium aluminium hydride (19 g, 0.5 mol) in

\* For details of Supplementary Publications, see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20.

<sup>12</sup> A. H. Ford-Moore and J. H. Williams, *J. Chem. Soc.*, 1947, 1465.

<sup>13</sup> W. Gee, R. A. Shaw, and B. C. Smith, *Inorg. Synth.*, 1967, 9, 19.

<sup>14</sup> (a) A. E. Arbusov, G. Kh. Kamaï, and O. N. Belorossova, *J. Gen. Chem. (U.S.S.R.)*, 1945, 15, 766; (b) T. H. Siddall, tert, and C. A. Prohaska, *J. Amer. Chem. Soc.*, 1962, 84, 3467.

redistilled tetrahydrofuran (350 ml). After 24 h at room temperature, the mixture was hydrolysed by cautious dropwise successive addition of water (20 ml), aqueous 15% sodium hydroxide (20 ml), and water (60 ml). The tetrahydrofuran solution was decanted from the precipitated solids, which were then washed with diethyl ether (*ca.* 100 ml). Solvents were removed from the combined tetrahydrofuran and diethyl ether solutions at *ca.* 25° and 40 mmHg. Vacuum distillation of the residue gave the *diphosphine* (VI) (7.0 g, 34%), b.p. 87–88° at 0.1 mmHg [Found: C, 56.3; H, 6.9; P, 36.4%; *M* 170 (mass spec.). C<sub>8</sub>H<sub>12</sub>P<sub>2</sub> requires C, 56.5; H, 7.1; P, 36.5%; *M*, 170].

*2,2'-(Phenylphosphinediyl)bisethylphosphine* (II).—A mixture of phenylphosphine<sup>15</sup> (11.0 g, 0.1 mol), diethyl vinylphosphonate (33 g, 0.2 mol), catalytic potassium *t*-butoxide (see before), and redistilled tetrahydrofuran (*ca.* 150 ml) was boiled under reflux for 16 h after the initial exothermic reaction had subsided. Tetrahydrofuran was then removed at *ca.* 25° and 35 mmHg; other volatile materials were distilled off up to 120° and 0.1 mmHg. The distillation residue exhibited  $\tau$  2.84 (Ph), 8.2br (P-CH<sub>2</sub>-CH<sub>2</sub>-P), and 6.06 (quintet, *J ca.* 7 Hz) and 8.73 (t, *J ca.* 7 Hz) (Et) (relative intensities *ca.* 5 : 4 : 8 : 12, respectively).

A solution of this adduct in redistilled tetrahydrofuran (250 ml) was treated with lithium aluminium hydride (19 g, 0.5 mol) in portions. After the vigorous reaction had subsided the mixture was boiled under reflux for 7 h, stirred for *ca.* 16 h at room temperature, then hydrolysed at 0° by successive cautious addition of water (20 ml), aqueous 15% sodium hydroxide (20 ml), and water (60 ml). The ethereal solution was decanted and the precipitated solids were washed liberally with more ether. The ether was removed from the combined solutions at *ca.* 25° and 40 mmHg, and the residue was vacuum distilled to give the *triphosphine* (II) (12.5 g, 55%), b.p. 106–109° at 0.1 mmHg, purified by a second vacuum distillation [Found: C, 52.1; H, 7.4; P, 40.3%; *M* (mass spec.), 230. C<sub>10</sub>H<sub>17</sub>P<sub>3</sub> requires C, 52.2; H, 7.4; P, 40.4%; *M*, 230].

*2,2',2''-Phosphinetriyltrisethylphosphine* (III).—Potassium *t*-butoxide (*ca.* 0.6 g) in boiling tetrahydrofuran (500 ml) was saturated with phosphine [prepared by dropping aqueous dioxan into a slurry of aluminium phosphide (total used 14 g, 0.24 mol) in dioxan]. The system was assumed to be saturated with phosphine when the calcium hypochlorite trap for the effluent vapour began to heat up and when cloudy vapour appeared in the flask. At this point, dropwise addition of di-isopropyl vinylphosphonate (92 g,

0.48 mol) was begun while the generation of phosphine was continued. After all the di-isopropyl vinylphosphonate had been added (*ca.* 90 min), the mixture was boiled under reflux for an additional 3 h in a phosphine atmosphere. The tetrahydrofuran was then removed at 35° and 35 mmHg. The <sup>1</sup>H n.m.r. spectrum of the residue (CDCl<sub>3</sub> solution) indicated the presence of isopropoxy-groups and PCH<sub>2</sub>CH<sub>2</sub>P units in *ca.* 2 : 1 ratio.

A solution of this adduct in diethyl ether (200 ml) was added to lithium aluminium hydride (40 g, 1.05 mol) in diethyl ether (500 ml). Smooth and vigorous evolution of gas occurred. After stirring for 68 h at room temperature the mixture was hydrolysed by successive addition of water (40 ml), aqueous 15% sodium hydroxide (40 ml), and water (120 ml). The ethereal solution was decanted from the precipitated solid and evaporated. Vacuum distillation of the residue gave a liquid (15 g) boiling up to 125° at 0.5 mmHg. Redistillation gave a forerun (3–4 ml), b.p. 40–45° at 0.15–0.2 mmHg, followed by the *tetraphosphine* (III) (9.6 g, 28%), b.p. 104–105° at 0.2 mmHg [Found: C, 33.9; H, 8.4; P, 57.7%; *M*, 214 (mass spec.). C<sub>8</sub>H<sub>18</sub>P<sub>4</sub> requires C, 33.6; H, 8.4; P, 57.9%; *M*, 214].

*3,6-Diphenyl-3,6-diphosphaoctane-1,8-diylidiphosphine* (IV).—A mixture of di-isopropyl vinylphosphonate (23.1 g, 0.12 mol), 1,2-bis(phenylphosphino)ethane<sup>10</sup> (13.5 g, 0.055 mol), and redistilled tetrahydrofuran (150 ml) was treated with small amounts (*ca.* 0.1 g) of potassium *t*-butoxide until the reaction began (as indicated by a yellow colour and heat evolution). The mixture was boiled under reflux for 6 h. Solvent was then removed at *ca.* 35° and 35 mmHg leaving a syrupy residue, the <sup>1</sup>H n.m.r. spectrum of which (CDCl<sub>3</sub> solution) exhibited phenyl, isopropoxy, and P-CH<sub>2</sub>-CH<sub>2</sub>-P resonances of relative intensities *ca.* 5 : 7 : 6.

A solution of this crude adduct in diethyl ether (200 ml) was added to lithium aluminium hydride (8 g, 0.21 mol) in diethyl ether (*ca.* 500 ml). After stirring at room temperature for 48 h, basic hydrolysis followed by distillation as for the tripod tetraphosphine (III) gave the *tetraphosphine* (IV) (6.6 g, 36%), b.p. 200–205° at 0.35–0.45 mmHg (Found: C, 59.1; H, 7.2; P, 33.8. C<sub>18</sub>H<sub>26</sub>P<sub>4</sub> requires C, 59.0; H, 7.1; P, 33.9%).

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<sup>15</sup> W. Kuchen and H. Buchwald, *Ber.*, 1958, **91**, 2296.