Synthesis of the Parent Phosphinine and Phosphaalkyne by Flash Thermolysis of Vinyldiallyl- and Triallyl-phosphine

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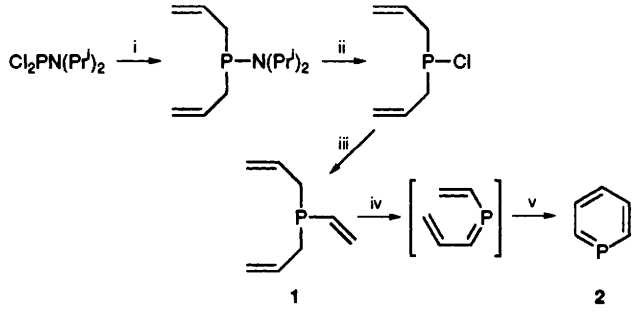
The parent phosphinine is obtained in *ca.* 40% yield by thermolysis of vinyldiallylphosphine at 700 °C at 10^{-3} Torr; under the same conditions, triallylphosphine mainly yields HC≡P which can be purified by trap-to-trap distillation.

The renewed interest in the coordination chemistry of the parent phosphinine[1] led us to wonder if it was possible to replace the original synthesis of this molecule[2] by a more convenient approach. In a previous paper,[3] we have shown that the electrocyclisation of a phosphahexatriene unit readily leads to a dihydrophosphinine. The problem, then, was to devise a simple access to unsubstituted 1-, 2- or 3-phosphahexatriene. The recent work of Ocando-Mavarez *et al.* on the synthesis of *C*-unsubstituted 1-phosphadienes by thermolysis of diallylphosphines[4] provided a possible solution.

Starting from dichloro(diisopropylamino)phosphine, we first devised, *via* a three-step sequence, a synthesis of vinyldiallylphosphine **1**† with an overall yield of 45%. This phosphine was directly evaporated from its tetraglyme solution into a flash vacuum thermolysis (FVT) tube.‡ The FVT of **1** at 700 °C and 10^{-3} Torr using a 6 mm tube produced the parent phosphinine **2** almost exclusively (Scheme 1). The

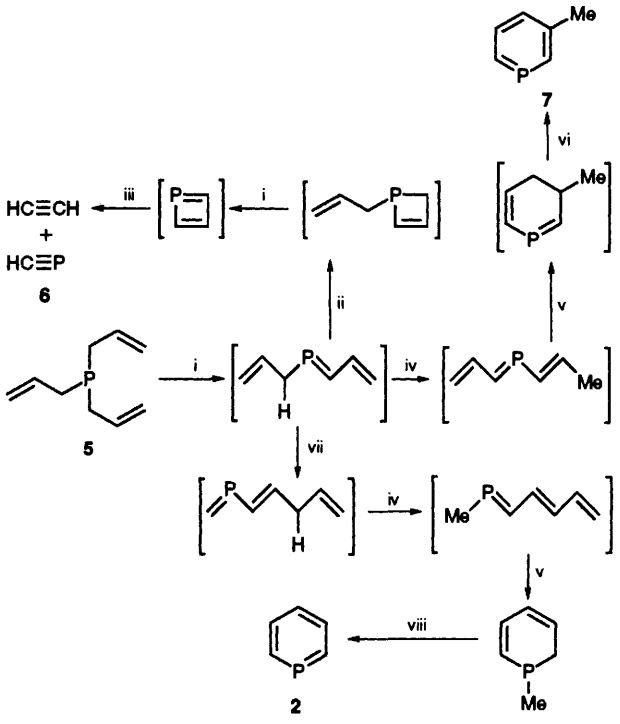


1 **2**

Scheme 1 *Reagents and conditions*: i, CH_2=CH–CH_2–MgBr, thf, 0 °C; ii, HCl, Et_2O, 0 °C; iii, CH_2=CH–ZnCl, tetraglyme, 0 °C; iv, 700 °C, 10^{-3} Torr; v, $-H_2$

† *Spectroscopic data*: **2**: ^{31}P NMR (81.01 MH_3) (CH_2Cl_2): δ −28.5. **4**: ^{31}P NMR (thf): δ +170.7, $^1J(^{31}P-^{183}W)$ 258.7 Hz; ^{13}C NMR (50.32 MHz) ($CDCl_3$): δ 127.4 [d, ^3J(C–P) 34.2 Hz, C-4), 138.4 [d, ^2J(C–P) 16.9 Hz, C-3 + C-5], 150.1 [d, ^1J (C–P) 18.5 Hz, C-2 + C-6], 195.2 [d, ^2J (C–P) 10.0 Hz, cis CO], 199.3 [d, ^2J (C–P) 28.9 Hz, *trans* CO]; ^{1}H NMR (200.13 MHz) ($CDCl_3$): δ 7.43 [m, ^4J (H–P) 6.9 Hz, ^3J (H–H) 8.2 Hz, ^4J (H–H) 0.9 Hz, 4-H), 7.85 [m, ^3J (H–P) 21.5 Hz, ^3J (3-H–2-H) 10.3 Hz, ^4J (3-H–5-H) −3.1 Hz, ^5J (3-H–6-H) 0.7 Hz, 3-H + 5-H], 8.43 [m, ^2J(H–P) 24.7 Hz, ^4J (2-H–6-H) 1.7 Hz, 2-H + 6-H); mass spectrum (EI, 70 eV, ^{184}W): *m/z* 420 (M^+, 30%), 364 (M^+ −2CO, 52%), 336 (M^+ − 3CO, 35%), 308 (M^+ −4CO, 48%), 279 (M^+ −5CO − H, 100%).

‡ The FVT experiments were performed in a quartz tube: internal diameter 4, 6 or 8 mm, length of the heated zone 40 cm. Initial vacuum *ca.* 10^{-3} Torr (1 Torr = 133.322 Pa), Alcatel vacuum pump, model 2063. The products were collected in a trap cooled at −196 °C and analysed by ^{31}P NMR spectroscopy at room temperature.



Scheme 2 *Reaction types*: i, retroene elimination of propene; ii, 4π-electrocyclisation; iii, [2 + 2] cycloreversion; iv, H [1,5] sigmatropic shift; v, 6π-electrocyclisation; vi, aromatisation by loss of H_2; vii, vinyl [1,5] shift; viii, aromatisation by loss of CH_4

$$[M(PC_5H_5)(CO)_5]$$
$$3\ M = Mo$$
$$4\ M = W$$

phosphinine **2** was characterized by ^{31}P NMR spectroscopy and as its *P*-bonded $Mo(CO)_5$[5] and $W(CO)_5$ complexes **3** and **4**.† Assuming quantitative complexation of **2** by $[M(CO)_5(thf)]$ (thf = tetrahydrofuran), the yield of **2** from **1** is *ca.* 40%; the pyrolysis of 2.5 g of **1** led to 2.85 g of complex **4**, corresponding to 0.65 g of phosphinine **2**.

For comparison, we also studied the FVT of triallylphosphine **5** under the same conditions as those used for **1** (8 mm tube). Surprisingly, HC≡P **6** was formed as the major product. Several phosphinines were observed as by-products, the two major ones being the parent phosphinine **2** and 3-methylphosphinine **7**.[6] The crude HC≡P in diethyl ether solution was purified by evaporation from a trap kept at −40 °C to a trap kept at −196 °C. All the phosphorus-containing side-products were thus removed and acetylene remained as the sole impurity. Scheme 2 depicts the proposed mechanism for the formation of **2**, **6**, and **7** from triallylphosphine. Most of the reactions are well precedented.[7] This synthesis of HC≡P compares favourably with the other available methods.[8]

Received, 15th March 1993; Com. 3/01491F

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