

Synthesis of Phosphapropyne by Flash Thermolysis of 1-Vinylphosphirane or Divinylphosphine

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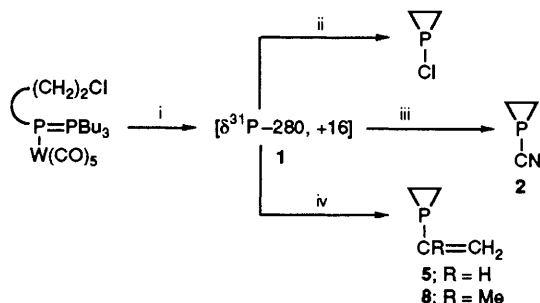
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The thermolysis of 1-vinylphosphirane **5** at 700 °C yields phosphapropyne **7**; owing to the existence of an equilibrium between divinylphosphine **6** and 1-vinylphosphirane above 500 °C, the same phosphapropyne is also obtained by thermolysis of divinylphosphine.

We have recently described a synthesis of the previously unknown parent 1-chlorophosphirane.¹ This product provides an access to a large variety of C-unsubstituted phosphiranes by reaction with various nucleophiles. The thermal stability of these products is relatively low and, in principle, their decomposition may proceed through the cleavage of the two P-C bonds of the ring, from cleavage of only one such bond or from ring expansion.² In order to shed some light on this problem, we decided to study the flash vacuum thermolysis (FVT) of some of these compounds.

We first prepared 1-cyanophosphirane **2**† by reaction of silver cyanide with the precursor of 1-chlorophosphirane **1**† (Scheme 1).

The FVT of **2**‡ produced several interesting results. At 500 °C, most of the starting material was recovered, although approximately 10% isomerisation into cyano(vinyl)phosphine **3** was found. At 700 °C, complete decomposition was observed. When a toluene or tetramethylethylene carrier was used, cyanophosphine **4**† was the major product (up to 50% yield)



Scheme 1 Reagents and conditions: i, heat, 25 °C, THF; ii, HCl, 25 °C; iii, AgCN, tetraglyme, then distillation into a trap at -196 °C, yield 90%; iv, $\text{CH}_2=\text{CR}-\text{MgBr}$, tetraglyme, then distillation into a trap at -196 °C, yield 70–90%; THF = tetrahydrofuran

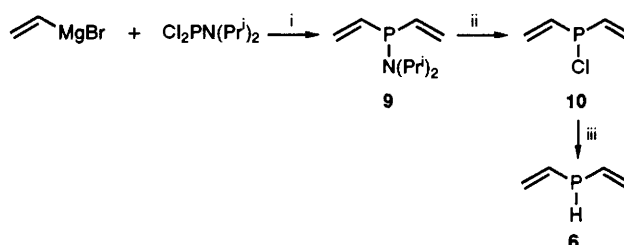
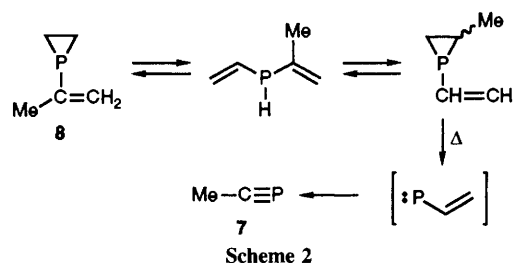
† Spectroscopic data (in C_6D_6 unless stated otherwise) **2**: ^{31}P NMR: δ -288; ^{13}C NMR: δ 11.3 [d, $^1\text{J}(\text{C}-\text{P})$ 37 Hz, CH_2], 124.9 [d, $^1\text{J}(\text{C}-\text{P})$ 114 Hz, CN]. **3**: ^{31}P NMR: δ -107.5 [d, $^1\text{J}(\text{P}-\text{H})$ 237 Hz]; ^{13}C NMR: δ 122.8 [d, $^2\text{J}(\text{C}-\text{P})$ 7.5 Hz, CH_2], 153.3 [d, $^1\text{J}(\text{C}-\text{P})$ 25.8 Hz, CH]. **4**: ^{31}P NMR: δ -195.0 [t, $^1\text{J}(\text{P}-\text{H})$ 220 Hz]. **5**: ^{31}P NMR: δ -241.0; ^{13}C NMR: δ 8.67 [d, $^1\text{J}(\text{C}-\text{P})$ 37.8 Hz, CH_2-P], 129.07 [d, $^2\text{J}(\text{C}-\text{P})$ 31.7 Hz, $=\text{CH}_2$], 144.15 [d, $^1\text{J}(\text{C}-\text{P})$ 38.3 Hz, $=\text{CH}-\text{P}$]; $\text{W}(\text{CO})_5$ complex of **5**: ^{31}P NMR: δ -193, $^1\text{J}(\text{P}-^{183}\text{W})$ 262 Hz; ^{13}C NMR: δ 10.73 [d, $^1\text{J}(\text{C}-\text{P})$ 10.6 Hz, CH_2-P], 134.61 [d, $^2\text{J}(\text{C}-\text{P})$ 13.8 Hz, $=\text{CH}_2$], 135.99 [d, $^1\text{J}(\text{C}-\text{P})$ 25.7 Hz, $=\text{CH}-\text{P}$]; mass spectrum (EI, 70 eV, ^{184}W): m/z 410 (M^+ , 36%), 270 ($\text{M}^+ - 5\text{CO}$, 79%), 240 (100%). **6**: ^{31}P NMR (THF): δ -62.0 [d, $^1\text{J}(\text{P}-\text{H})$ 225.7 Hz]. **7**: ^{31}P NMR (toluene): δ -60.8 [q, $^3\text{J}(\text{H}-\text{P})$ 15.5 Hz], see ref. 6. Compound **7** was also characterized as [3 + 2] cycloadducts with $\text{HC}(\text{N}_2)(\text{COOEt})$ and $\text{Mes}-\text{C}\equiv\text{N}-\text{O}$, see ref. 8. **8**: ^{31}P NMR: δ -228.0. **9**: ^{31}P NMR (diethyl ether): δ +29.7. **10**: ^{31}P NMR (diethyl ether): δ +78.7. **11**: mixture of three isomers: ^{31}P NMR: δ -68.3, $^1\text{J}(\text{P}-\text{H})$ 207 Hz; δ -87.5, $^1\text{J}(\text{P}-\text{H})$ 199.5 Hz (major isomer); δ -105.4, $^1\text{J}(\text{P}-\text{H})$ 209 Hz. **12**: ^{31}P NMR (toluene): δ -61.8 [t, $^3\text{J}(\text{H}-\text{P})$ 14.8 Hz].

‡ The FVT was performed in a quartz tube: internal diameter 4 or 6 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 in solution at room temp.

along with traces of **3**, with better yields of **4** being obtained with tetramethylethylene than with toluene. The simplest way to rationalize these observations is to postulate that **2** decomposes by loss of ethylene to give the cyanophosphinidene ($\text{N}\equiv\text{CP}$), which tends to give polymeric products. If a carrier is used, the triplet phosphinidene³ abstracts hydrogen from it to give **4** and, consistently, the yield of **4** increases with the ability of the carrier to release hydrogen atoms. It must be stated here that the very recent work of Gaspar and coworkers has produced strong evidence for the production of phosphinidenes by thermal or photochemical decomposition of phosphiranes.⁴ An early Russian work stated that $\text{N}\equiv\text{C}-\text{PH}_2$ **4** rearranges in basic medium (liq. NH_3 + NaNH_2) to give $\text{H}_2\text{N}-\text{C}\equiv\text{P}$.⁵ In a preliminary attempt to clarify that point, we treated **4** by a catalytic amount of DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) in THF at -78 °C, but observed only a polymerization of **4** and no detectable quantity of the postulated phosphalkyne.



Our next series of experiments dealt with 1-vinylphosphirane **5**† (Scheme 1). At 500 °C, **5** produced only divinylphosphine **6**† which was identified by comparison with an authentic sample (see below). At 700 °C, **6** was no longer formed and the only detectable product was phosphapropyne **7**.† Taking into account our previous results and the data of ref. 4, the most logical mechanism relies on a vinylphosphinidene to phosphapropyne isomerization. In line with the observations of Denis *et al.*,⁶ we find that phosphapropyne is stable at room temp. for at least one week in solution. The instability of **7**, which was observed by other authors must be due to the presence of HCl, which is generally formed as a by-product (e.g. in the thermolysis of EtPCL_2 ^{7,8}).



Scheme 3 Reagents and conditions: i, THF, 0 °C; ii, HCl, diethyl ether, 0 °C; iii, LiAlH_4 in excess, tetraglyme, -78 °C then evaporation onto a cold finger at -196 °C

Somewhat unexpectedly, the thermolysis of 1-(prop-2-enyl)phosphirane **8**[†] at 700 °C also produced mainly phosphapropyne **7** (Scheme 2). This result led us to suspect the existence of an equilibrium between 1-vinylphosphiranes and divinylphosphines. In order to establish this point, we prepared divinylphosphine **6** using the chemistry depicted in Scheme 3.

Mixtures containing both **5** and **6** were obtained upon pyrolysis of pure samples of **5** or **6** at 500 °C, thus establishing the existence of an equilibrium between these two species at elevated temperature. The formation of phosphapropyne **7** from **8** then can be rationalized as depicted in Scheme 2. Quite logically, the thermolysis of **6** at 700 °C proved to be a synthetically viable route to phosphapropyne **7** in essentially pure form.

An additional interesting observation was made when replacing **6** by its deuterio analogue. D-P(CH=CH₂)₂ at 700 °C produced mainly **7** with only traces of the deuterio analogue DCH₂-C≡P. This observation is easily rationalized by the postulated phosphinidene mechanism.

Finally, we decided to check whether it was possible to use this kind of approach to prepare higher homologues such as EtC≡P. Owing to the existence of an equilibrium like the one depicted in Scheme 2, the synthesis of EtC≡P required the symmetrical bis(propen-1-yl)phosphine **11** as starting material. Phosphine **11**[†] was prepared from Cl₂PNEt₂ using the same chemistry as for **6**. The FVT of the crude isomeric mixture at 700 °C indeed yields EtC≡P **12**[†] as the major product but substantial dealkylation to HC≡P also occurs.⁹ Since **11**, contrary to **6**, also decomposes to give significant

amounts of PH₃, this synthesis of EtC≡P has no synthetic value.

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