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Flash Vacuum Pyrolysis of Dichlorophosphines over Magnesium: Generation and Reactivity of Simple Phosphinidenes

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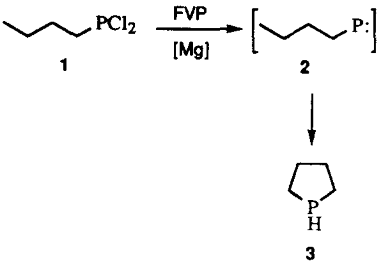
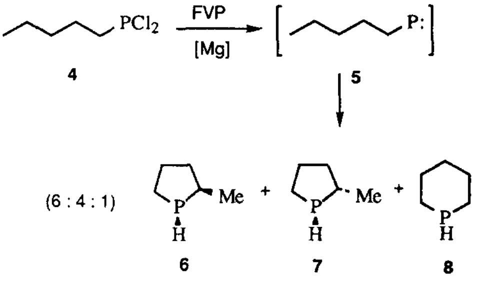
Abstract: Flash vacuum pyrolysis of dichlorophosphines over magnesium at 500–600 °C gives the products expected from intramolecular CH insertion of the corresponding phosphinidenes.

There has been considerable recent interest in phosphinidenes, R–P:, both from an experimental[1] and theoretical[2] point of view, and the first direct observation of a triplet phosphinidene was recently reported.[3] An obstacle to the fuller understanding of the chemistry of these species is the lack of convenient routes for their generation. Gas phase methods have proved very useful in the generation of a variety of low-valent reactive phosphorus compounds,[4] and recent examples include the formation of phosphaalkenes by flash vacuum pyrolysis (FVP) of α-chlorophosphines over potassium carbonate.[5] The thermal decomposition of primary alkyldichlorophosphines results in loss of 2 HCl to give phosphaalkynes at 750–900 °C.[6] In 1989 Bock reported the pyrolysis of $MePCl_2$ and $EtPCl_2$ over magnesium powder to give a range of products attributable to surface-adsorbed phosphinidenes,[7] but in this study no products were isolated and their identification rests on photoelectron and mass spectroscopic analysis. We recently described the use of flash vacuum pyrolysis over freshly resublimed magnesium as an efficient and preparatively useful method for dehalogenation of organic halides.[8] We were interested to see whether application of the same method to higher dichlorophosphines would allow a study of the reactivity of simple alkylphosphinidenes and perhaps provide a preparatively useful method for phosphorus heterocycles.

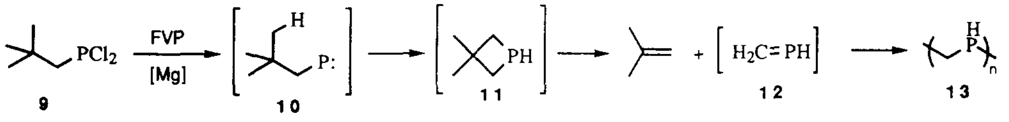
When butyldichlorophosphine **1** was subjected to FVP over magnesium at 600 °C using the method described previously,[8] the major product was but-1-ene identified by NMR and GC-MS comparison with an authentic sample. However the ^{31}P NMR spectrum revealed the presence of a phosphorus-containing product with δ_P –71.0, which was shown by comparison of the non proton-decoupled spectrum as well as the ^{13}C NMR and GC-MS data[9] with literature values to be phospholane **3**. The yield was approximately 5%. This seems most likely to arise from intramolecular CH insertion of butylphosphinidene **2** as shown, and this reactivity is in notable contrast to that of the corresponding nitrene which undergoes a 1,2-hydrogen shift to give propionaldehyde imine.[12] In view of this result, it was of interest to examine pentyldichlorophosphine where a





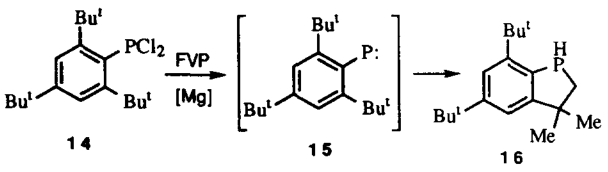
similar process could give either a five- or six-membered ring. FVP of **4** over magnesium at 600 °C again gave largely the hydrocarbons pent-1-ene and decane identified by ^{13}C NMR and GC-MS. The phosphorus-containing products, again obtained in around 5% yield, consisted of a 6 : 4 : 1 ratio of three secondary phosphines which were readily identified by comparison with literature data[13] as *cis*-2-methylphospholane **6**, *trans*-2-methylphospholane **7** and phosphinine **8**, respectively. Thus pentylphosphinidene **5** also undergoes intramolecular CH insertion under these conditions with a high although not complete selectivity for the five- as opposed to the six-membered ring products.

The predominance of apparent 1,2-elimination to give hydrocarbon products in these cases relies on the presence of a β-hydrogen atom and to avoid this neopentyldichlorophosphine **9** was examined. Under the same conditions as before this gave isobutene, isolated in 42% yield despite its volatility, and a highly air-sensitive grey pyrophoric solid which gave analytical data in reasonable agreement with expectation for the phosphaethene polymer **13**.[17] Formation of a polymer from **12** has been noted before but it was not characterised.[18] These products probably result from formation of neopentylphosphinidene **10** which can undergo intramolecular insertion to give the phosphetane **11** which then fragments to isobutene and **12**. Despite its extreme reactivity, the polymer **13** is indefinitely stable when stored under dry CH_2Cl_2 and its potential applications, particularly after controlled oxidation, are currently being evaluated.



Attempts to extend this route to simple arylphosphinidenes such as PhP: were frustrated by facile reorganisation of the groups at phosphorus with $PhPCl_2$, for example, giving Ph_2PCl and Ph_3P together with some white phosphorus, presumably from dechlorination of the resulting PCl_3. The occurrence of this process on pyrolysis without magnesium was noted some time ago.[19] Better results were achieved with the hindered tri-*tert*-butylphenyl compound **14**. The corresponding phosphinidene **15** has been generated by a number of routes including photolysis of the corresponding diphosphene, ArP=PAr,[20] and photolysis or thermolysis of the bis-azide, $ArP(N_3)_2$,[21] and is well known to undergo intramolecular CH insertion leading to the phosphaindane **16**. FVP of **14** over magnesium at 600 °C gave only tri-*tert*-betylbenzene but when the temperature was reduced to 500 °C this was accompanied by **16** formed in a yield of 20%.[22]

The use of this approach to generate aminophosphinidenes, R_2N–P: was also examined but FVP of Et_2N–PCl_2 over magnesium at 600 °C again led to intervention of a 1,2-elimination process to afford the imine MeCH=NEt[24] together with Et_2NH and white phosphorus. The use of more sterically hindered bis-silyl compounds such as $(Bu^tMe_2Si)_2N$–PCl_2[25] lacking a β-hydrogen should overcome this problem and is currently being investigated.



14 **15** **16**

$$\underset{\mathbf{17}}{Et_2N-PCl_2} \xrightarrow[\text{[Mg]}]{\text{FVP}} \underset{\mathbf{18}}{MeHC=NEt} + P_4$$

Finally it should be noted that, although the insertion products obtained are those which might be expected from free gas-phase phosphinidenes, the generation of the intermediates adsorbed on the metal surface may affect their reactivity. We similarly noted[8] that 1,1-dichloroalkanes often give products different from those expected from free carbenes.

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9 Selected analytical and spectroscopic data (NMR data are for solutions in C_6D_6 unless otherwise stated and coupling constants J are in Hz): 3: ν_{max} /cm^{-1} 2320 and 2250 (P–H); δ_P –71.0 (d of t of t, J_{PH} 187, 22, 7) [lit.,[10] (neat) –66.2 (d, $^1J_{PH}$ 189)]; δ_C 19.6 (d, J 8) and 30.2 (d, J 6) [lit.,[11] 21.2 (d, J 10) and 31.6 (d, J 5)]; m/z 88 (M^+, 55%) and 60 (100).

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13 **6**: δ_P –44.6 (d of m, $^1J_{PH}$ 180) [lit.,[14] –46.6 (d of m, $^1J_{PH}$ 190); **7**: δ_P –54.7 (d of m, $^1J_{PH}$ 185) [lit.,[14] –56.6 (d of m, $^1J_{PH}$ 197); **8**: δ_P –65.4 (d of m, $^1J_{PH}$ 190) [lit.,[15] δ_P –66.0, lit.,[16] ($CFCl_3$) $^1J_{PH}$ 200±5].

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