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Generation and reactivity of a *3H*-phosphaindene: the first *3H*-phosphole

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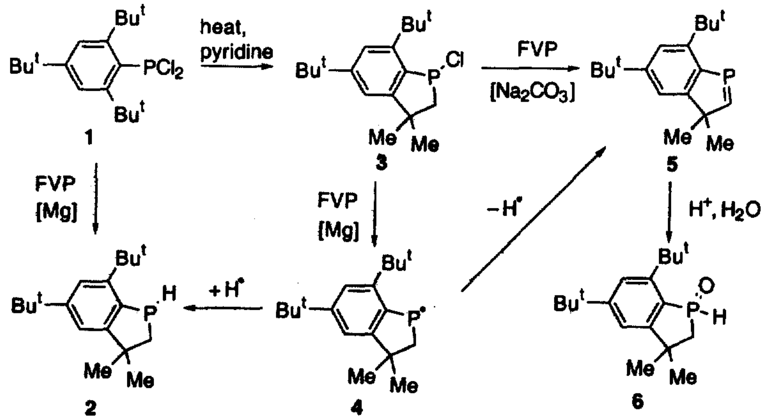
Abstract

By gas-phase pyrolysis over a solid base the title compound has been prepared as a 1:1 mixture with its hydration product and characterised spectroscopically; the hindered C=P double bond is surprisingly unreactive.

Keywords: Phospholes; Phosphaalkenes; Phosphorus heterocycles; Gas phase reactions

Since the pioneering report of Yoshifuji and coworkers in 1981,[1] the use of the 2,4,6-tri-*t*-butylphenyl and similar steric protecting groups has allowed access to a variety of low-valent phosphorus compounds. We recently reported that flash vacuum pyrolysis (FVP) of the dichlorophosphine **1** over magnesium produces the known phosphaindane **2**.[2] Although this can be rationalised by dechlorination of **1** to produce a surface-adsorbed phosphinidene which then undergoes intramolecular insertion into CH to afford **2**, a number of other mechanisms are possible. We describe here further studies on this system which have led to identification of the *3H*-phosphaindene **5**.

Careful examination of the product mixtures from FVP of **1** over magnesium under a variety of conditions revealed the presence of **2** and its known oxidation product **6** but also a further minor phosphorus-containing product to which we assign the structure **5**. The three products were clearly distinguished by their ^{31}P and ^{1}H NMR spectra [**2**: δ_P −79.7 (d, J 183),



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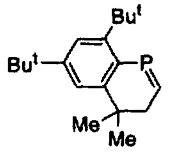
6: δ_P +30.5 (d, *J* 465), **5**: δ_P +222.25 (d, *J* 37); **2**: δ_H 4.45 (ddd, *J* 181, 12, 8, PH), **6**: δ_H 8.04 (ddd, *J* 466, 3.6, 2.4, PH), **5**: δ_H 8.36 (d, *J* 37, C*H*=P)] and were present in a ratio of 20:10:1. An alternative explanation for the conversion of **1** into **2** is removal of HCl by the magnesium to give the *P*-chloro compound **3** and then dechlorination and abstraction of H by the resulting phosphinyl radical **4**. In order to examine this possibility, **3** was prepared using the reported method involving heating **1** in the presence of pyridine.[3] When **3** was subjected to FVP over magnesium at 500 °C the same three products **2**, **6** and **5** were formed but the ratio was now 6:1:1. We interpret this reaction as proceeding by magnesium induced dechlorination of **3** to give the phosphinyl radical **4** which may then either abstract a hydrogen atom to give **2** or lose a hydrogen atom to give **5**. The formation of **6** may be explained either by oxidation of **2** or by hydration of **5** by adventitious oxygen or moisture respectively. This rather unexpected result led to the realisation that the efficient conversion of **3** into **5** might be achieved by FVP over a solid base rather than a dehalogenating agent. A similar approach has been used by Denis and coworkers to gain access to a wide range of low-valent phosphorus compounds,[4] including, most recently, the formation of acyclic phosphaalkenes by FVP of α-chlorophosphines over solid potassium carbonate.[5] When **3** was subjected to FVP over a bed of anhydrous sodium carbonate at 400 °C, the product consisted of a 1:1 mixture of **5** and **6**.[6] Although we have so far found it impossible to obtain **5** in pure form, or to obtain its tungsten pentacarbonyl complex for X-ray crystallographic studies, the increase in its abundance from 3% in the initial pyrolysis of **1** to 50% here has allowed its spectroscopic characterisation[8] and a preliminary study of its reactivity.

Although *1H*-phospholes are well known[9] and there have been a few reports of *2H*-phospholes,[10] there appears to be no previous report of a *3H*-phosphole. The spectroscopic data obtained do however provide good evidence for the structure **5** with the values of δ_P and $^2J_{PH}$ being in good agreement with those observed for acyclic phosphaalkenes[5] while the value of δ_H 8.36 for CH=P compares well with those for **7** (δ_H 8.03),[11] the phosphaindole **8** (δ_H 8.53),[12] the diphosphaindene **9** (δ_H 8.42)[13] and *3H*-indole **10** (δ_H 8.40).[14] More



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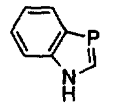

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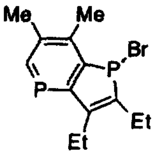

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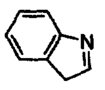

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convincingly, almost complete assignment of the ^{13}C NMR spectrum was possible and the data for **5** were in excellent agreement with those for the homologue **7** whose preparation by intramolecular insertion of the tri-*t*-butylphenylphosphanylidenecarbene was reported while our work was in progress.[11] Unexpected features common to the spectra of both compounds include phosphorus coupling to only one of the ring protons and a substantial (presumably through-space) coupling between phosphorus and the protons of the *ortho* *t*-butyl group. The most obvious difference is in the value of δ_C for C=P of 192.2 for **5** as compared to 168.3 for **7** which has obviously been greatly affected by introduction of the extra methylene group although the values of $^1J_{CP}$ at 33 Hz is almost the same as for **7** (34 Hz). Using GCMS the mass spectrum of **5** could be obtained from the mixture of **5** and **6** and it showed the expected molecular ion although high resolution measurement was not possible.

Since the phosphine oxide **6** is relatively inert it was possible to conduct a preliminary study of the reactivity of **5** using the 1:1 mixture of **5** and **6**. Calculations have shown that the C=P bond of phosphaalkenes is likely to be relatively non-polarized leading to the possibility of addition in either sense.[15] Rather surprisingly, **5** appears to be resistant towards hydrolysis under neutral conditions and shaking a C_6D_6 solution of **5** and **6** with water led to no change in the ratio of the two components. On the other hand addition of one drop of dilute sulfuric acid led to immediate and complete conversion of **5** into **6**. Since the phosphinidenium ion resulting from *C*-protonation is obviously susceptible to attack by water, we attempted addition of HCl which would give **3**, but even with the most stringent precautions to exclude moisture, passage of dry HCl gas through the solution of **5** and **6** led only to gradual conversion of **5** into **6** with no sign of **3** or any other new product. The phosphaindene **5** was found to be similarly inert towards anhydrous ammonia and methanol and also towards cycloaddition with 2,3-dimethylbuta-1,3-diene or diazomethane. We conclude that the C=P double bond in **5** is very highly hindered and that this feature, which allows it to exist in solution with no tendency to dimerise, also makes it unreactive towards addition and cycloaddition with hydration to give **6** being the only process so far observed.

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[6] *Preparation of* **5**: Using the equipment for flash vacuum pyrolysis as described previously,[7] the furnace tube was filled with a 5 cm bed of anhydrous sodium carbonate between glass wool plugs and and heated at 400 °C and 10^{-3} Torr for 2 h. The inlet tube containing **3** (ref. 3) (0.66 g) was then attached and the pyrolysis carried out at 400 °C and 10^{-3} Torr for 1 h. The system was isolated from the vacuum and filled with dry nitrogen. The cold trap was allowed to warm to room temperature, sealed off and carefully dried and transferred to a nitrogen-filled dry-box. The colourless solid consisting of a 1:1 mixture of **5** and **6** was dissolved out using C_6D_6.

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[8] *Spectroscopic data* for **5**: δ_P (121.4 MHz): +222.25 (d, $^2J_{PH}$ 37); δ_H (300 MHz) 8.36 (1 H, d, $^2J_{PH}$ 37), 7.48 (1 H, dd, J_{HH} 2, J_{PH} 2), 7.32 (1 H, d, J_{HH} = 2), 1.60 (9 H, br s), 1.53 (6 H, br s) and 1.31 (9 H, s); δ_C (75 MHz) 192.2 (d, *J* 33, P=*C*), 123.8 (d, *J* 43, P–*C*), 121.0 (d, *J* 5, Ar*H*), 117.0 (d, *J* 2, Ar*H*), 58.0 (d, *J* 13, CMe_2), 36.8 (CMe_3), 33.1 (CMe_3), 32.0 (d, *J* 11, CMe_3), 31.3 (CMe_3) and 27.0 (d, *J* 8, CMe_2) [position of remaining three quaternary aromatic carbons uncertain]; *m/z* (GCMS) 274 (M^+, 7%), 259 (5), 232 (12), 218 ($M^+ - C_4H_8$, 32), 176 (14), 162 ($M^+ - 2 \times C_4H_8$, 28) and 57 (100).

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