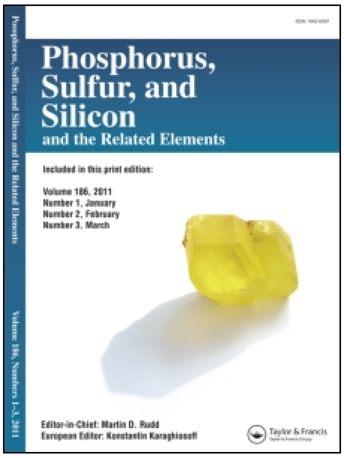

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SUBSTITUTED DIHYDROPHOSPHININES, SYNTHESIS AND BASE-INDUCED ISOMERISATION

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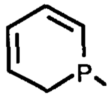
Abstract The synthesis of α-chloro-tetrahydrophosphinines by inter- or intramolecular [4+2] cycloaddition reactions involving unstabilized phosphaalkenes is presented. Conditions for a selective base-induced isomerisation of substituted dihydrophosphinines are precised. A tautomeric phosphaalkene/vinylphosphine equilibrium was for the first time evidenced.

INTRODUCTION

While a number of substituted dihydrophosphinines of structure **1** or **2** have been reported in the literature[1], any representant of the other three expected isomers **3-5** have been to our knowledge described.



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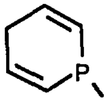

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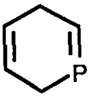

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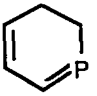

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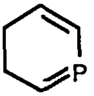

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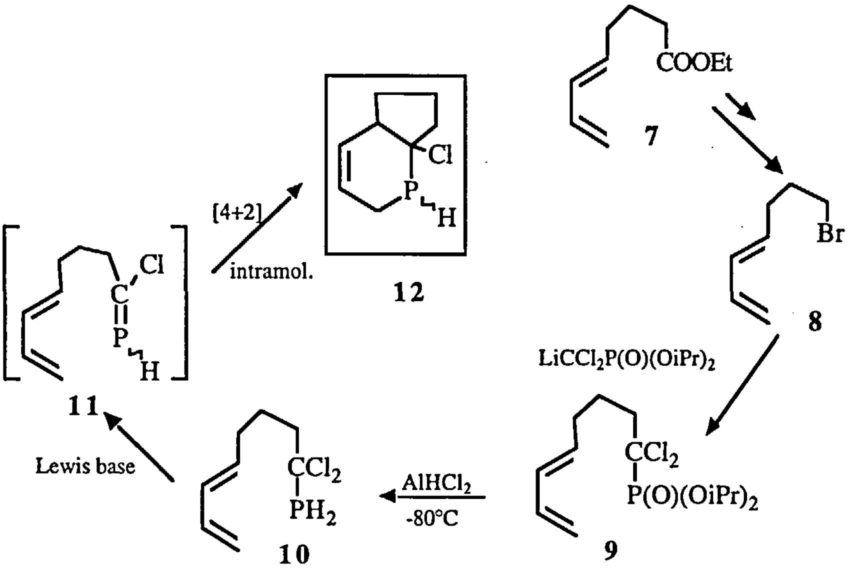
Since phosphaalkene/vinylphosphine transformations and reverse reactions are well known processes[2], isomerisation of the dihydrophosphinines **1-5** can be consequently expected. We present in this work the formation of the two differently substituted transient 2,5-dihydrophosphinines **7** and **19** (derivatives of structure **3**) by dehydrohalogenation of the corresponding α-chlorophosphine precursors **6** and **12** and we precise the conditions for their base-induced isomerisation (formation of derivatives of structure **1** or **4**).

RESULTS

The first α-chlorophosphine precursor **6** has been synthesized according to the literature procedure by a [4+2] cycloaddition of dimethylbutadiene with the transient phosphaalkene (Cl)CH=P-H, easily formed by a selective monodehydrochlorination of α,α'-dichlorophosphine in the presence of an excess of pyridine (yield 70%)[3]. The second α-chlorophosphine precursor **12** is formed according to the sequence outlined in Scheme 1. The bromoheptadiene **8** was first obtained by reduction of **7**[4] followed by a mesyl/bromine exchange. The dichlorophosphonate **9** is then formed by condensation of the dichloroalkyllithium derivative on **8**. The dichlorophosphine **10** obtained by chemoselective reduction of **9** cannot be distillated. After hydrolysis and filtration, the crude mixture is treated by an excess of pyridine. A selective monodehydrochlorination slowly occurs at room temperature and the phosphaalkene intermediate **11** was trapped by a stereoselective intramolecular [4+2] cycloaddition. The α–chlorophosphine **12** was obtained in 80% overall yield.



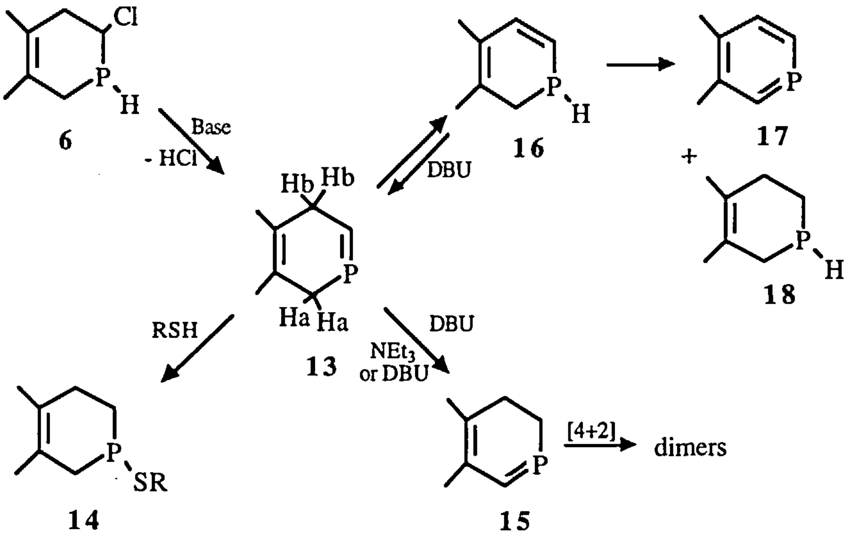
Scheme 1

Obtention of the adducts **14** and **20** by dehydrochlorination of **6** and **12** respectively with Et_3N in the presence of a large excess of iPrSH indicates that the 2,5-dihydrophosphinines **13** and **19** are the primary products. Consequently, the following reactions realized by treatment of **6** or **12** with various Lewis bases in absence of thiol have formally **13** and **19** as starting material (Schemes 2 and 3).

In the presence of Et_3N, the rearrangement of the dihydrophosphinine **13** into the dihydrophosphinine **15** is observed. The characteristic ^{31}P NMR signal of this intermediate[5] ($\delta = 226$ ppm) slowly decreases. Finally, a clean dimerization [4+2] cycloaddition) is observed (presence of two isomers in 85:15 molar ratio). These results are in good agreement with the generally observed behaviour of the 1-phosphabutadiene structures. [5]

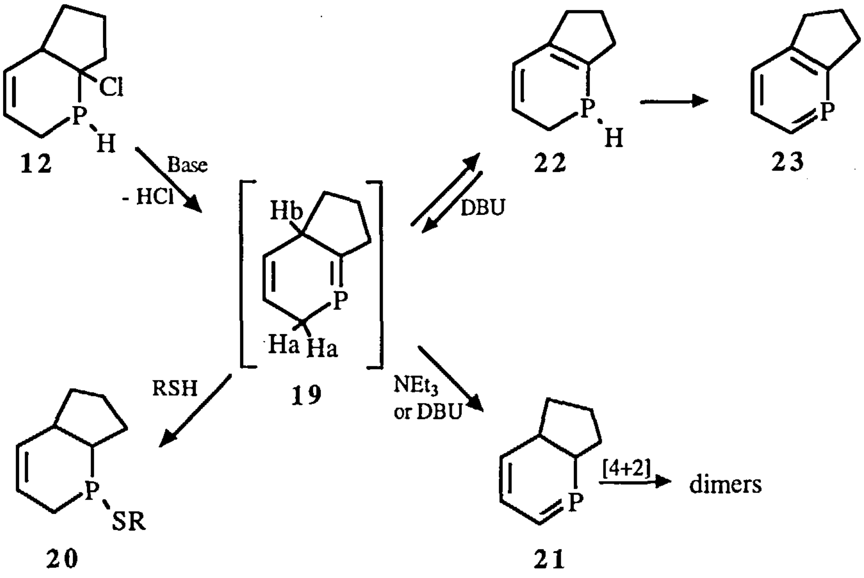
In the presence of DBU, the dihydrophosphinine intermediate **13** rearranges into a new isomer, the 1,2-dihydrophosphine **16** (δ = -114 ppm; $^1J_{PH}$ 197 Hz). This product is stable during few hours (NMR at room temperature) . However, a disproportionation was observed[6] during the purification leading to a mixture of phosphinine **17** and tetrahydrophosphinine **18.** These compounds were characterized by comparison of the NMR data with those of authentic samples. [7,8] The selectivity of the rearrangement of **13** is consequently depending on the strenght of the Lewis base.

We have elsewere observed the formation of the thiophosphine **14** by addition of iPrSH onto the phosphinine **16** in the presence of a catalytic amount of DBU. This result indicates that **16** rearranges into the isomeric structure **13.** A tautomeric equilibrium vinylphosphine/phosphaalkene is thus for the first time evidenced.



Scheme 2

Similar rearrangements were observed by treatment of the bicyclic phosphaalkene **19** with various Lewis bases. The structures of the observed isomers were depending on the strenght of the base (Scheme 3). The transient phosphabutadiene isomer **21** (δ_P = 187) observed after addition of Et_3N rapidly dimerized (presence of 5 isomers which are not fully characterized). The other dihydrophosphinine isomer **22** was observed by addition of DBU. This phosphine (δ_P = -114, $^1J_{PH}$ 190 Hz) can be analyzed at room temperature by NMR but is too unstable to be isolated in pure form ; a partial oxidation to the bicyclic phosphinine **23** (δ_P =193) is observed. A tautomeric vinylphosphine/phosphaalkene equilibrium was also observed (formation of **20** by addition of thiol on **22**).



Scheme 3

In conclusion, unknown dihydrophosphinines were characterized and the conditions for their base-induced isomerization precised. Intramolecular [4+2] cycloadditions should allowed to introduce unstabilized phosphaalkenes as powerful tools in the synthesis of complexe structures.

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