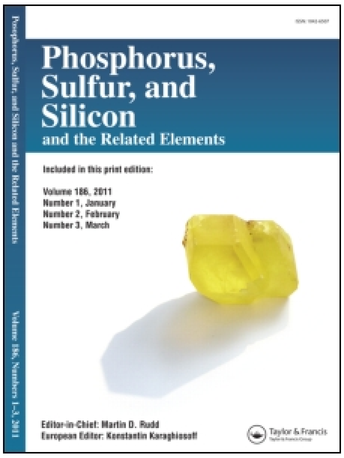

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Efficient Synthesis of Unstabilized Phospha-alkenes by Stereoselective Lewis Base-Induced Rearrangement of Vinylphosphines

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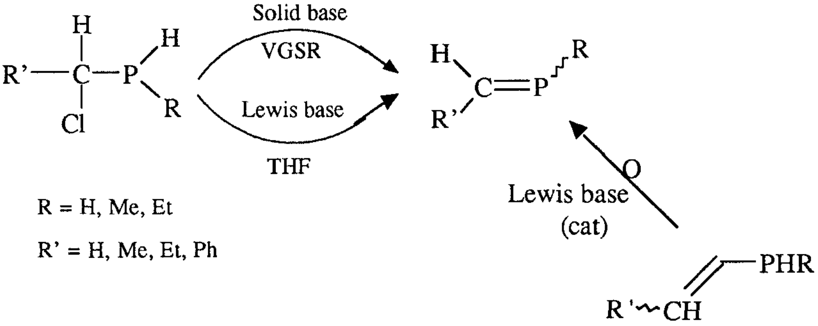
Abstract : Vinylphosphines are synthesized by reduction of the corresponding vinyl-phosphonic or phosphinic esters and by P-alkylation of the vinylphosphine parent compound **1**. They rearrange into phospha-alkenes in the presence of a catalytic amount of a strong Lewis Base. The transient species are characterized by chemical trapping.

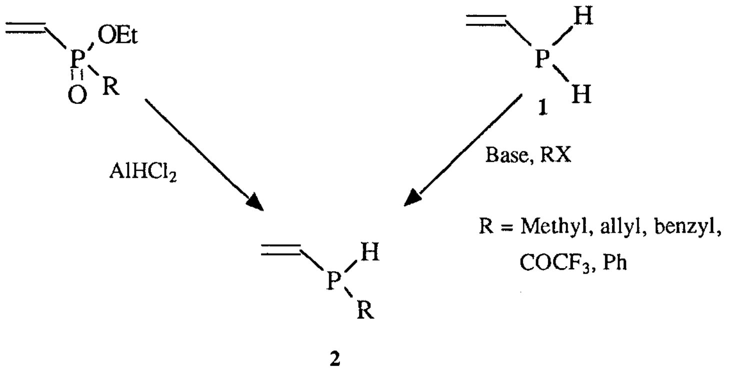
Due to the high reactivity of the P=C double bond, the main synthetic routes to phospha-alkenes already described in the literature are related to the kinetically stabilized derivatives(1). We have already reported that unhindered phospha-alkenes can be prepared by HCl- elimination of α-chlorophosphines either in solution by using a Lewis base or in the gas-phase in a Vacuum Gas-Solid Reaction (VGSR) with K_2CO_3 as a solid base(2) (Scheme 1).



Scheme 1

We present here another approach which consists in rearranging primary or secondary vinylphosphines into the corresponding phospha-alkenes in the presence of a catalytic amount of a strong Lewis base.

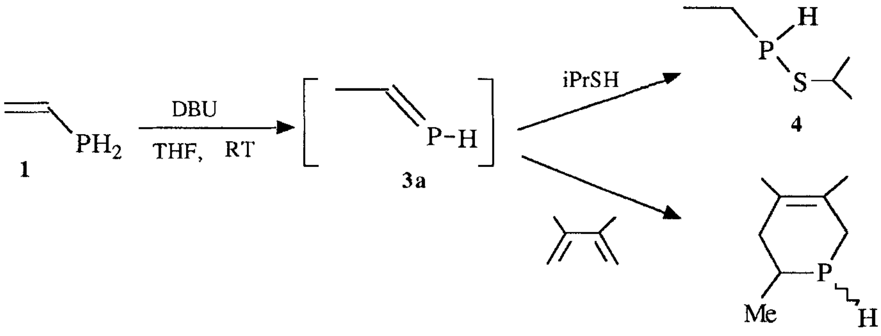
The primary and secondary vinylphosphine precursors are intrinsically reactive species and consequently have been for a long time very poorly investigated(3). The fact that the parent compound **1** which has been recently prepared by FVT of the anthracenic adduct(4) presents a reasonable stability emphasized the synthetic potential of this class of compounds. We have prepared the primary and secondary derivatives on gram-scale by chemoselective reduction of the corresponding vinylphosphonic(5) and phosphinic esters(6) with $AlHCl_2$ as an electrophilic reducing agent. The secondary vinylphosphines **2** were also efficiently synthesized by deprotonation of the parent compound **1** with potassium trimethylsilanolate ($KOSiMe_3$) followed by alkylation of the phospha-allylanion intermediate (Scheme 2). The yields of the reaction are ranged between 62 and 76%(6).



Scheme 2

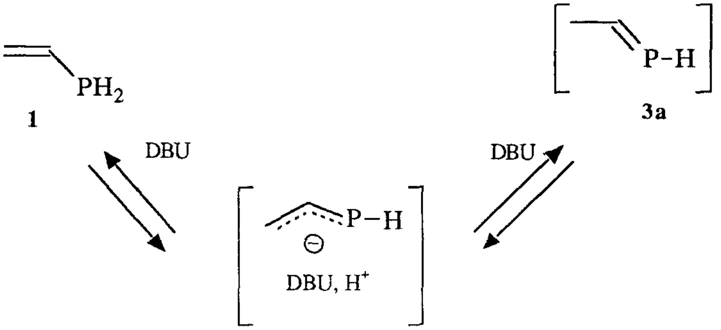
Vinylphosphines **2** thus prepared present a rather good stability ; they can generally be stored in the refrigerator in the presence of a small amount of hydroquinone.

Unlike enols and enamines, very little is known about the rearrangement of vinylphosphines. The only published example concerns the formation of a kinetically stabilized phospha-alkene upon heating the corresponding vinylphosphine(7). We detected only traces of the cycloadduct **5** upon heating **1** at 50°C during 2 days in the presence of dimethylbutadiene, products of self-condensation being mainly observed. A similar result was observed when a weak Lewis base like pyridine or NEt_3 was introduced in the reaction mixture. However, the reaction changes dramatically by introducing a catalytic amount of a strong Lewis base (DBU) : the rearrangement occured at room temperature and the yield in cycloadduct **5** became higher than 78% (Scheme 3).



Scheme 3

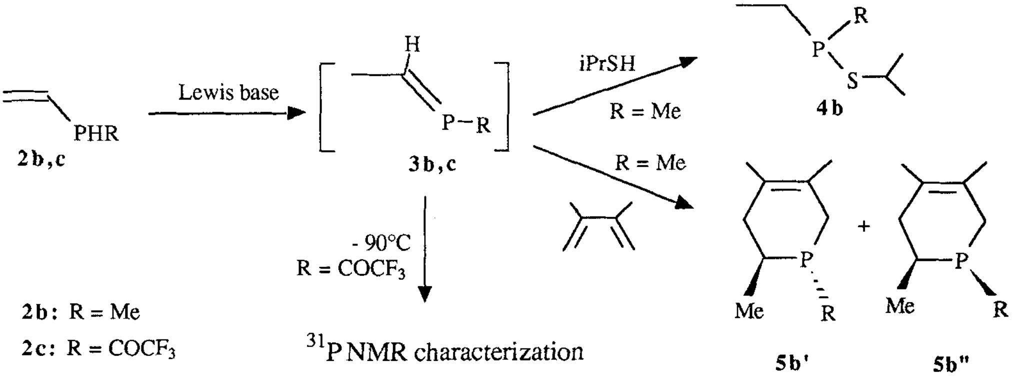
In attempt to explain this result, we supposed that the remarkable acidifying effect of the carbon-carbon double bond, already observed for ethenol and ethenamine(8), is sufficient to induce a proton transfer from the phosphine to the Lewis base (Scheme 4).



Scheme 4

Whatever the conditions, we never detect by low temperature ^{31}P NMR the presence of the transient phospha-allylanion or the phospha-alkene **3a**, the concentration of these two species being probably too low. These high dilution conditions minimize the self-condensation of a transient species which is known to polymerize around -140°C(2a). The high yield observed in the cycloadduct **5** shows the synthetic potential of this approach.

This rearrangement was then extended to secondary alkyl- and acylvinylphosphines **2b** and **2c**. Due to the lower PH acidity of the phosphine **2b**, the rate of the reaction was much slower. Interestingly, the rearrangement was found to be stereoselective ; thus, chemical trapping of ethylidenephosphine **3b** with dimethylbutadiene led to the formation of the two cycloadducts **5b'** er **5b''** in *ca* . 97/3 molar ratio. However, we cannot precise at this stage the sterochemisty of the main isomer (Scheme 5).



Scheme 5

The stereochemistry was however established for the P-acylphosphaalkene **3c** which is sufficiently stable to be observed by low temperature ^{31}P NMR ($\delta_P = 210.8$ ppm). The E-configuration was assigned on the basis of the low value of the $^2J_{PH}$ coupling constant (19.9 Hz)(9).

In conclusion, the base induced rearrangement which has been previously observed with compounds bearing an oxygen or a nitrogen directly bonded to an ethylenic function can be extended to the corresponding phosphorus derivatives. This reaction constitutes a new and efficient approach to stabilized and unstabilized phospha-alkenes.

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