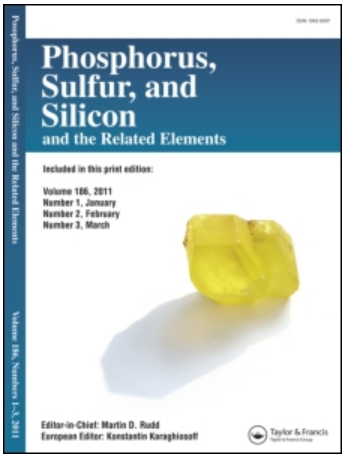

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Application of Phosphaalkenes and Phosphaalkynes in Organophosphorus Chemistry, New Results

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Free phosphaalkenes are prepared by stereocontrolled rearrangement of vinylphosphines and β-elimination of α,α'-dichloroalkylphosphines. Synthetic potential is evaluated in inter- and intramolecular [4+2] cycloadditions.

INTRODUCTION

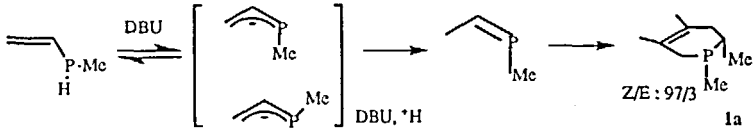
We developed since few years two general routes to phosphaalkenes and phosphaalkynes. The first one involves HCl-elimination of α-chloroalkylphosphines and the second rearrangement (1,3-hydrogen shift) of α-unsaturated phosphines.[1,2] This procedure is of a particular interest since the corresponding phosphonate or phosphinate precursors are easily available by anionic routes and since the reduction to the desired phosphines by $AlHCl_2$ is chemoselective.[2] The first works concerned the formation under vacuum of the simplest derivatives at the surface of a solid base (vacuum gas-solid reactions) and their characterisation in gas-phase (HRMS, PES) and in solution after trapping the transient species on a cold finger (low temperature NMR).[1,2] We are now investigating the reactivity of such species in solution in order to evaluate the synthetic potential of these two approaches. The results presented in the following mainly concern phosphaalkenes.

RESULTS

Vinylphosphine/phosphaalkene route

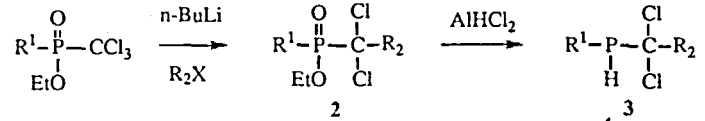
Phosphaalkene (Me)CH=P-Me, formed by base-induced rearrangement of P-methylvinylphosphine with DBU can be trapped in a [4+2] cycloaddition by dimethylbutadiene or cyclohexadiene to lead to the tetrahydrophosphine and phosphanorbornene adducts **1a,b** respectively (mixture in both cases of 2 diastereoisomers in 97:3 molar ratio). The yield is higher than 75% (Eq 1)[3]. The

observed value of the $^2J_{PC}$ coupling (15.4 Hz) for **1a** is in favor of a *trans* relationship between the lone pair and carbon of methyl group.[4-7] To explain this stereoselectivity, we assume that the rearangement involves in the first step the fomation of a mixture of transient *endo* and *exo* phosphaallyl anions, in equilibrium with the vinylphosphine precursor. The major adduct **1a** is formed by cycloaddition of the *cis* phosphaalkene resulting from the protonation of the thermodynamically more stable[8] *endo* conformation.



Phosphalkenes by HCl-elimination route

The phosphaalkenes formed by β-elimination of 1-chloroalkylphosphines present in most the cases a poor synthetic interest : the stability of the unsaturared intermediates is weak, yields of the cycloadducts are usually low and elimination is not steroselective.[1] Since it is well known that chlorine substitution stabilizes phosphaalkenes[9], we decide to choose chlorophosphakenes as a new target. The dichlorophosphinate precursors **2a-c** are easily formed by a sequence involving halogen/metal exchange starting from trichlorophosphinate[2b] followed by C-alkylation of the intermediate.[10,11] Chemoselective reduction of esters **2a-c** with $AlHCl_2$ in THF afforded to the expected free phosphines **3a-c**.

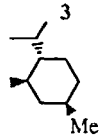


2a R^1 = Ph, R^2 = Et

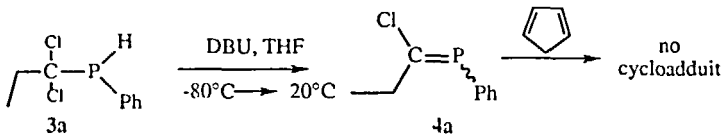
2b R^1 = Ph, R^2 = CH_2=CH-CH=CH-$(CH_2)_3$-

2c R^1 = L-Men, R^2 = Et

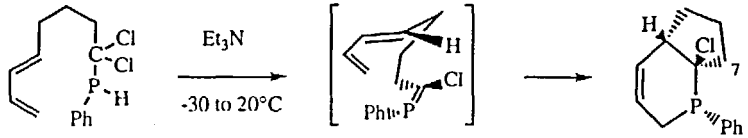
L-Men =



HCl-elimination of **3a** with DBU (-80 to 20°C) leads to the phosphaalkene isomers **4a** (2 isomers in 45:55 molar ratio). These intermediates are as expected strongly stabilized (τ1/2 1h30 at RT in THF solution) as compared with the very low stability of the unchlorinated derivative EtCH=PPh (decomposition above -70°C).[1b, 3] Its reactivity is however weak towards dienes since no cycloadduct is observed with cyclopentadiene.

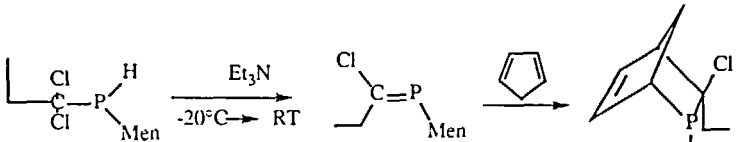


Elimination of the 1,3-heptadiene dichlorophophine 3b with NEt_3 (-30 to 20°C) leads directly to the phosphabicyclononene adduct 5b resulting from a [4+2] intramolecular cycloaddition. The following observations : high overall yield (>80%), non detection of the phosphalkene intermediate 4b and absence of products resulting of self-condensation, are consistent with entropic activation. Only one isomer is observed.[11] The $^2J_{PC}$ (15 Hz) is consistent with a *trans* relationship between the lone pair and C(7)[4-7]. The cis-fused cycloadduct is proposed to take into account the preference for cycloaddition with the P-substituent in *endo* position[12].



3b 4b 5b

The dehydrochlorination of the P-menthylphosphine 3c (pyridine, Et_3N or DBU) is also highly stereoselective; the sole phosphaalkene 4c observed (δ_P 240 ppm, stereochemistry at this time not precised) presents a fairly stability ($\tau_{1/2}$ = 24h in solution at 20°C). When the elimination occurs in the presence of an excess of cyclopentadiene (best results with Et_3N at 0°C), the major cycloadduct 5c is observed (δ_P = 37.7, 68%), beside three other minor isomers (δ_P = 46.9, δ_P = 23.1, δ_P = 21.7) in 8:11:13 molar ratio respectively. The structure of these products is actually not fully established. These first results are consitent with a selectivity of the Diels-Alder reaction (the preference of the P substituent in *endo* position is expected[12,13]) and with a face selectivity (a *si* face selectivity induced by L-menthyl substituant on phosphaalkene complexes has been observed by Mathey and co-workers[13]). Thus, a prochiral free phosphalkene bearing an optically active group on phosphorus can be used as starting material for the direct synthesis of optically active phosphines. This new synthetic approach opens interesting prospects.

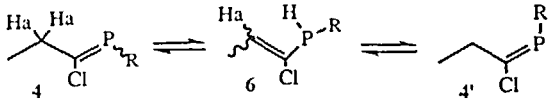


3c 4c 5c

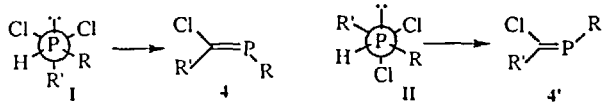
On the mechanism of b-elimination of dichlorophosphines 3a-3c

We have observed a mixture of two phosphalkenes by β-dehydrohalogenation of 3a and only one derivative in the elimination of 3b and 3c. A Z-E isomerisation and formation of the more stable product is unlikely since the calculated energy barrier to internal rotation of a free alkylphosphaalkene is close to 49 Kcal, a higher value than that of the complexed counterpart (25 Kcal)[14]. A mechanism involving a stereocontrolled base-induced phosphalkene/vinylphosphine tautomerism induced by

allylic protons cannot be rule out. However, we never observed the phosphalkenes 4a,4a'(R = Ph) by treatment of 6a[10] with various Lewis bases.



Control of the sterochemistry in the β-elimination of dichlorophosphines is more likely coming from a preferred conformation of the phosphine 3c. Only the conformers I and II are involved with the favoured anti-elimination.



In summary, phosphaalkenes can be formed by two stereoselective approaches, rearrangement of vinylphosphines and β-elimination of α,α'-dichloroalkylphosphines. The formation of a bicyclic free phosphine as a major product in cycloaddition of P-menthylphosphalkene with cyclopentadiene evidences the stereocontrol and face selectivity of the [4+2] cycloadditions. Application of free phosphaalkenes as useful reagents in asymmetric synthesis is thus expected.

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