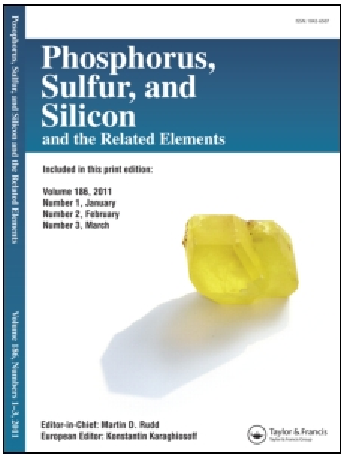

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis of Primary α,α'-Dichlorophosphines, Precursors of Unhindered C-Chlorophospha-alkenes and Synthetic Equivalents of λ³-Phospha-alkynes

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To cite this Article Denis, J. M. , Guillemin, J. C. and Guennec, M. Le(1990) 'Synthesis of Primary α,α'-Dichlorophosphines, Precursors of Unhindered C-Chlorophospha-alkenes and Synthetic Equivalents of λ³-Phospha-alkynes', Phosphorus, Sulfur, and Silicon and the Related Elements, 49: 1, 317 — 320

To link to this Article: DOI: 10.1080/10426509008038969

URL: http://dx.doi.org/10.1080/10426509008038969

Phosphorus, Sulfur, and Silicon, 1990, Vols. 49/50, pp. 317–320
Reprints available directly from the publisher

Printed in the United Kingdom

Synthesis of Primary α,α'-Dichlorophosphines, Precursors of Unhindered C-Chlorophospha-alkenes and Synthetic Equivalents of λ^3-Phospha-alkynes

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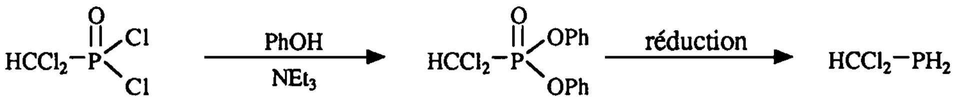
Abstract : α,α'-dichlorophophines, easily obtained by chemoselective reduction of the corresponding phosphonates, can be considered as precursors of unhindered C-chlorophosphaethylenes and synthetic equivalents of phospha-acetylenes.

In the last few years, various kinetically stable phospha-alkynes have been prepared and their reactivity has been investigated [1]. They can react with 1,3-dipoles [1,2], 1,3-dienes [3] and are used as new ligands in coordination chemistry [1,4]. Unhindered phospha-alkynes are only stable at low temperature and, with the exception of the parent compound H-C≡P [5,6] no efficient route is yet available. We describe the synthesis of α,α'-dichlorophosphines [7] and show that these species are precursors of unstabilized C-chlorophospha-alkenes and synthetic equivalents of λ^3-phospha-alkynes.

Dichloromethylphosphine 3a is easily prepared by esterification of the phosphonic acid dichloride 1 followed by chemoselective reduction of the phosphonate unit (Eq. 1).

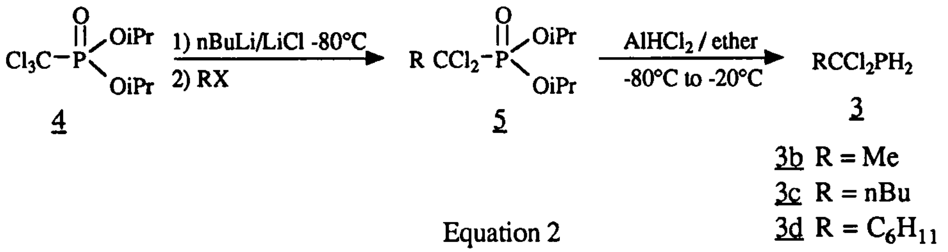


1 2 3a

Equation 1

The major problem was to determine the specific conditions of this reaction : dichloroalane ($AlHCl_2$) in suspension in tetraglyme or in diethylether is the electrophilic reducing agent which gives the best results leading to the phosphines 3a with 53% and 88% yield respectively [7,8].

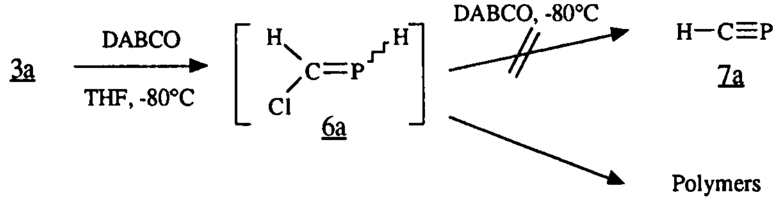
This reduction can be extended to the C-alkylated derivatives which are obtained by metallation-alkylation of the trichlorophosphonate 4 (yields > 80%) (Eq. 2).



Equation 2

α,α'-Dichlorophosphines 3 slowly polymerize at room temperature but can be kept for several weeks in the refrigerator in the presence of a small amount of hydroquinone.

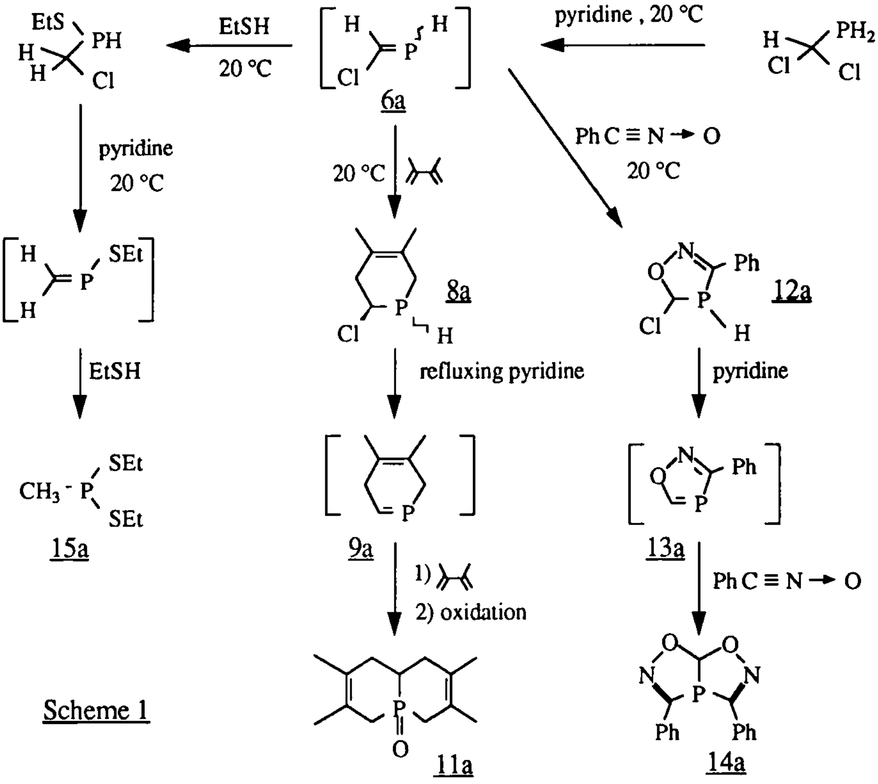
The HCl-elimination of phosphine 3a, performed with 1,4-diazabicyclo [2.2.2] octane (DABCO) in excess rapidly occurs from -80°C and only leads to polymers. The expected phosphaalkene 6a or phosphaalkyne 7a are never observed by low temperature ^{31}P NMR experiments. Since 7a is known to be stable below -20°C [5], polymers probably originate from 6a (Eq. 3).



Equation 3

The formation of intermediate 6a is unambiguously established by the following experiments.

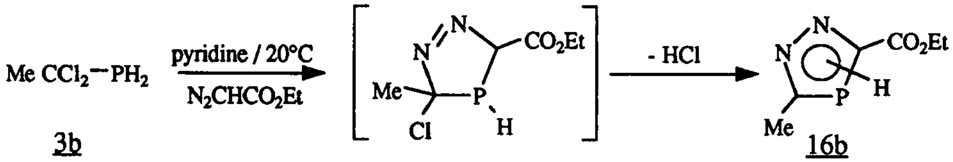
In the présence of dimethylbutadiene, the cycloadduct 8a is slowly formed at room temperature (12h) in pyridine as solvent and weak base (2 isomers : ^{31}P NMR -58.4 ppm and -72.7 ppm). The bis-adduct 10a is obtained by heating the same mixture in refluxing pyridine ($\delta^{31}P$ = -63.5 ppm) and then oxidized to 11a (H_2O_2) ($\delta^{31}P$ = 46.0 ppm). The dihydrophosphinine 9a which can formally be considered as a [4 + 2] cycloadduct of butadiene with H-C≡P is not observed. The C-chlorophosphaalkene intermediate 6a can also be trapped with benzonitriloxide in pyridine. The first cycloadduct 12a is not isolated, a second HCl-elimination fastly occurs, leading, via the transient phosphaisoxazole 13a, to the symetrical bis-adduct 14a in good yield (76%). The orientation of the cycloaddition is confirmed by ^1H and ^{31}P NMR ; the spectroscopic data are in a good agreement with those of an authentic sample recently prepared by Regitz and coll. in a bis-[3 + 2] cycloaddition of nitriloxide with H-C≡P (Scheme 1)[6].



Scheme 1

Finally, the unhindered phosphaalkene 6a can also be chemically trapped by a nucleophilic addition with ethanethiol. Isolation of the first adduct seems difficult : a second elimination competitive with the first one leads to the bis-adduct 15a.

Similar cycloadditions or nucleophilic additions are also observed with the transient C-alkyl intermediates 6b-6d. For example, the diazaphosphole 16b is obtained via a [3 + 2] cycloaddition with ethyl diazoacetate, the second HCl-elimination occuring spontaneously ($\delta^{31}P = 98.0$ ppm) (Eq. 4).



Equation 4

Both HCl-eliminations from dichlorophosphines 3 are selective. The first elimination occurs with a weak Lewis base leading to the transient C-chlorophospha-alkene 6 ; the second HCl-elimination occurs from the primary adduct. The intermediates 9a, 13a, 16b and the compounds 10a, 14a, can be considered respectively as the mono and diadducts of H-C≡P with dienes and dipoles.

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