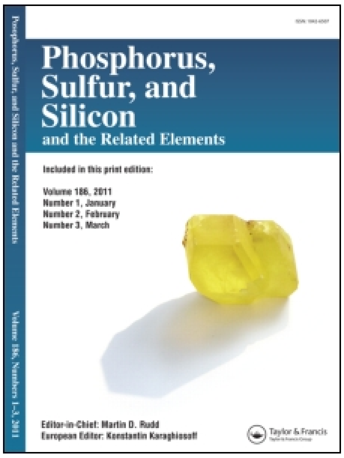

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# New Applications of Ph 3 P=N--Li in Organic Synthesis and Heteroatom Chemistry

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# NEW APPLICATIONS OF $Ph_3P{=}N{-}Li$ IN ORGANIC SYNTHESIS AND HETEROATOM CHEMISTRY

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*The lithium triphenylaminophosphonium azayldiide* ***1*** *proved again to be a very good tool in organic synthesis, allowing further synthesis of various compounds such as vinyl nitriles, aromatic or heteroaromatic nitriles, and mono-, bis-, and trisphosphinimines.*

*Keywords:* Azayldiide; metallated ylide; nitrile; triphosphinimine

## INTRODUCTION

As part of our works on metallated ylides showing reinforced nucleophilic activity, already illustrated in the case of the diphenylphosphonium diylides and diazaylides,[1–4] we present here our results concerning the reactivity and the new applications of a third category of this type of ylides: the lithium triphenylaminophosphonium azayldiide **1**.

$$Ph_3P{=}N{-}Li$$

**1**

Lithium azayldiide $Ph_3P{=}NLi$ **1** was until recently used mainly in coordination chemistry. It was initially prepared by Schmidbaur,[5] but we have developed a method allowing direct *one-pot* preparation in large scale, by double deprotonation of the corresponding aminophosphonium salt, which is obtained from gaseous ammonia and dibromophosphorane.[1,6]

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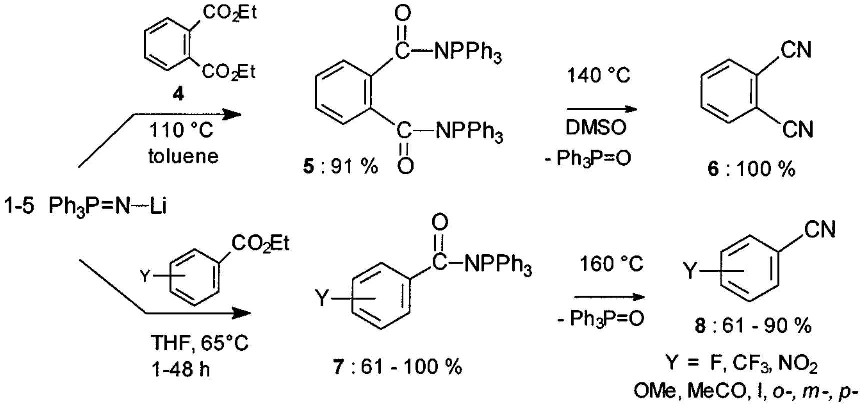
## RESULTS AND DISCUSSION

The study of the reactivity of **1** allowed us already to find numerous applications for this compound in organic synthesis.[1] For instance, we could develop new methods for the synthesis of (1) amines, (2) aminophosphonium salts precursors of aminoacids, (3) valuable precursors for the sulfonamide chemistry, (4) *N*-alkoxycarbonyl and *N*-acyltriphenylphosphinimines, and (5) $\alpha,\beta$-unsaturated nitriles.[1,7]

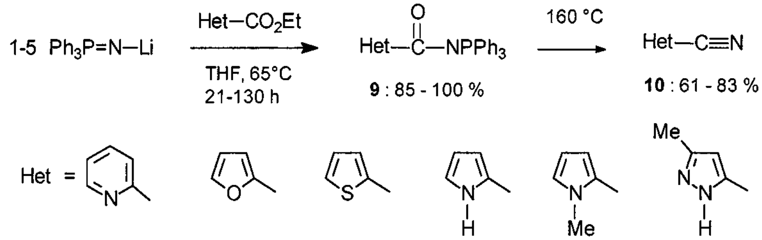
More recently, we observed that the diethyl phthalate **4** can be converted into the diphosphinimine **5** via nucleophilic substitutions at the carbonyl groups,[7] the corresponding dinitrile **6** being then obtained by intramolecular aza-Wittig reaction.



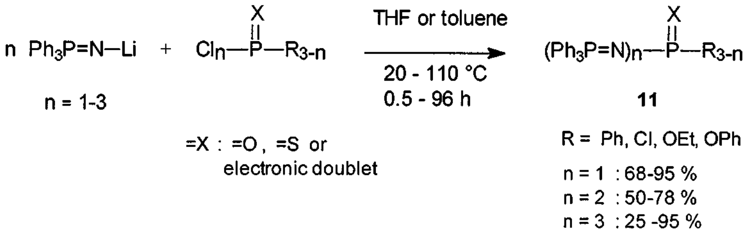
In the case of substituted ethyl benzoates the corresponding nitriles **8** can be obtained chemoselectively in good overall yields (61–90%) with various functional groups (F, I, $CF_3$, OMe, MeCO, and $NO_2$), wherever their position on the aromatic ring may be. Only the compounds with the nitro group in the meta or ortho position give a lower yield (20–28%).

It is noteworthy that the kinetic of the two steps of the nitrile synthesis are different depending on the nature of the substituents. The first step, the N-acylphosphinimines **7** formation, is accelerated by electronwithdrawing substituents and, on the contrary, slowed down by electron-donating groups. The reverse and stronger effects are verified for the second step, the intramolecular aza-Wittig reaction. Accordingly, the synthesis of nitriles from the corresponding esters is all in all favored by electron-donating substituents and not favored by electron-withdrawing substituents on the aromatic ring.

The method has also been successfuly extended to the *one-pot* synthesis of a large family of functionalized heteroaromatic nitriles **10**.



In another field, we have recently performed a systematic study of the reactivity of $Ph_3PNLi$ towards $P^{III}$ and $P^{IV}$ phosphorus electrophiles. The results show the possibility of obtaining (*one-pot*), in very good yields, a large range of N-substituted phosphinimines, which are valuable precursors for the (poly-)phosphazene chemistry. Thus, depending on the cases, mono-, di-, and also triphosphinimines **11** have been synthesized. Notice that for a same family of phosphorus electrophiles (X=: S=, O=, or electronic doublet), the trisubstitution is, as expected, more difficult to reach than the di- or the monosubstitution. Moreover, for a same number of chlorine on the starting phosphorus electrophile, the ease of substitution increases in the following order: $Cl_nP(S)R_{3-n} < Cl_nP(O)R_{3-n} \ll Cl_nPR_{3-n}$. Thus, sulfurated diphosphinimines were difficult to obtain and the corresponding sulfurated triphosphinimines impossible to reach. Notice that the triphosphinimine ($P^{III}$, $n = 3$) is a very basic compound which is similar to a Schwesinger's base.



$$n\ Ph_3P{=}N{-}Li + Cl_n{-}\overset{\overset{X}{\|}}{P}{-}R_{3-n} \xrightarrow[\text{20 - 110 °C, 0.5 - 96 h}]{\text{THF or toluene}} (Ph_3P{=}N)_n{-}\overset{\overset{X}{\|}}{P}{-}R_{3-n}$$

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