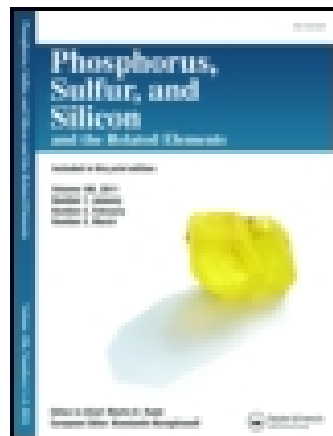


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New Applications of Ph₃P=N--Li in Organic Synthesis and Heteroatom Chemistry

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NEW APPLICATIONS OF $\text{Ph}_3\text{P}=\text{N}-\text{Li}$ IN ORGANIC SYNTHESIS AND HETEROATOM CHEMISTRY

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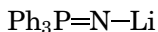
(Received July 29, 2001; accepted December 25, 2001)

*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**.



1

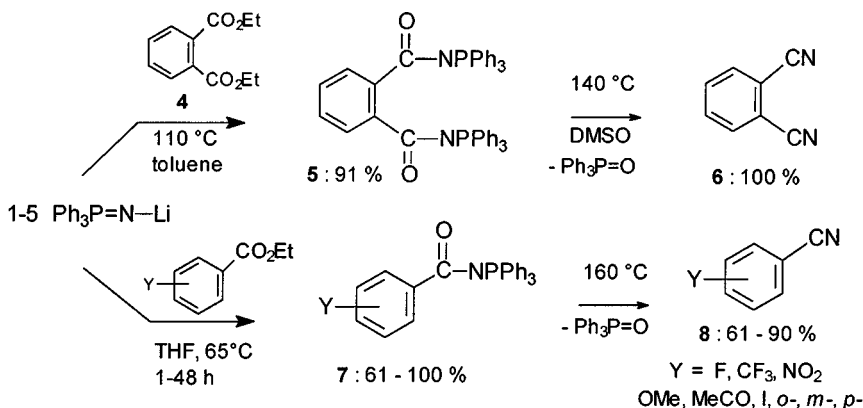
Lithium azayldiide $\text{Ph}_3\text{P}=\text{N}\text{Li}$ **1** was until recently used mainly in coordination chemistry. It was initially prepared by Schmidbaur,⁵ but we have developed a method allowing direct *one-pot* preparation in large scale, by double deprotonation of the corresponding aminophosphonium 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) α,β -unsaturated nitriles.^{1,7}

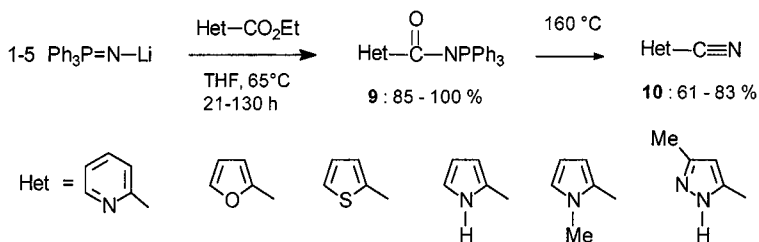
More recently, we observed that the diethyl phthalate **4** can be converted into the diphosphinimine **5** via nucleophilic substitutions at the carbonyl groups,⁷ the corresponding dinitrile **6** being then obtained by intramolecular aza-Wittig reaction.



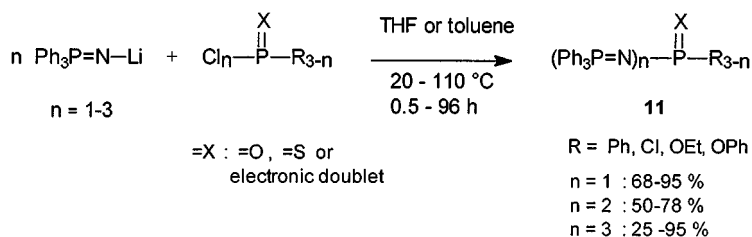
In the case of substituted ethyl benzoates the corresponding nitriles **8** can be obtained chemoselectively in good overall yields (61–90%) with various functional groups (F, I, CF₃, OMe, MeCO, and NO₂), wherever their position on the aromatic ring may be. Only the compounds with the nitro group in 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 successfully 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 ($\text{X} = \text{S} =, \text{O} =,$ 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: $\text{Cl}_n\text{P(S)}\text{R}_{3-n} < \text{Cl}_n\text{P(O)}\text{R}_{3-n} \ll \text{Cl}_n\text{PR}_{3-n}$. Thus, sulfurated diphosphinimines were difficult to obtain and the corresponding sulfurated triphosphinimines impossible to reach. Notice that the triphosphinimine ($\text{P}^{\text{III}}, n = 3$) is a very basic compound which is similar to a Schwesinger's base.



REFERENCES

- [1] H. J. Cristau, *Chem. Rev.*, **94**, 1299–1313 (1994).
- [2] (a) M. Taillefer, N. Inguibert, L. Jäger, K. Merzweiler, and H. J. Cristau, *Chem. Commun.*, 565–566 (1999); (b) M. Taillefer, H. J. Cristau, and I. Jouanin, *Synthesis*, 69–74 (2001).
- [3] (a) M. Taillefer, H. J. Cristau, A. Fruchier, and V. Vicente, *Journal of Organometallic Chemistry*, **624**, 307–315 (2001); (b) H. J. Cristau, I. Jouanin, and M. Taillefer,

- Journal of Organometallic Chemistry*, **584**, 68–72 (1999); (c) M. Taillefer and H. J. Cristau, *Tetrahedron Letters*, **39**, 7857–7860 (1998); (d) H. J. Cristau and M. Taillefer, *Tetrahedron*, **54**, 1507–1522 (1998).
- [4] L. Jäger, V. Maurizot, C. Wagner, M. Taillefer, and H. J. Cristau, *Challenges for Coordination Chemistry in the New Century*, 195–200 (2001).
- [5] H. Schmibaur and G. Jonas, *Chem. Ber.*, **100**, 1120–1128 (1967).
- [6] H. J. Cristau, E. Manginot, and E. Torreilles, *Synthesis*, 382–384 (1991).
- [7] H. J. Cristau, A. Hammami, and E. Torreilles, *Heteroatom Chemistry*, **10**, 49–54 (1999).