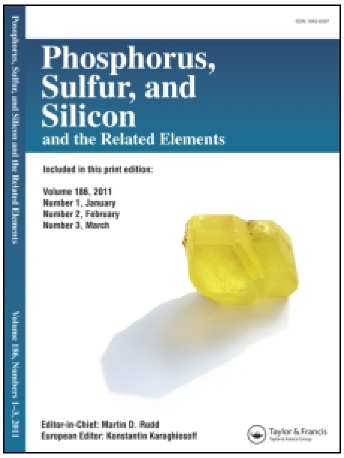

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PHOSPHONIUM DIAZA-DIYLIDS AND AZA-YLDIID AS NEW AND EFFICIENT REAGENTS FOR PRIMARY AND SECONDARY AMINES SYNTHESIS

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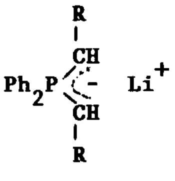
Abstract Metallated aminophosphonium ylids, diaza-diylids and aza-yldiid, are investigated as reagents for primary and secondary amines synthesis.

INTRODUCTION

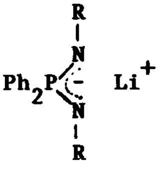
Metallated phosphonium ylids, either of the diylid 1 or the yldiid 2 types[1], are strong nucleophilic organophosphorus reagents which react easily with overcrowded ketones[2,3,4] and also with low electrophilic carbonyl compounds such as esters, carbonates, carbamates and thiocarbamates. In these cases a further Wittig reaction affords α,β-unsaturated ester or amide. Toward amides, reaction can be directed to give either the acylated phosphonium salts or, by selective monoprotonation of the betainic intermediate, the enamines as normal Wittig olefination products[5].



1

$Ph_3P{=}CH{-}Li$

2



3

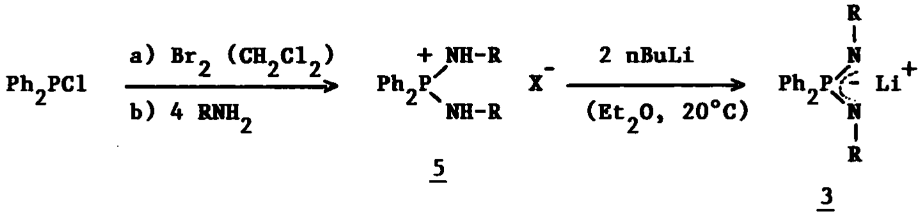
$Ph_3P{=}N{-}Li$

4

The enhanced nucleophilic reactivity of diylids 1 and yldiid 2 in regard to the corresponding monoylids led us promptly to investigate the reactivity of their aza-analogs 3 and 4.

Such reagents have been already described[6,7,8], but, till now, to our knowledge, their use as reagents for organic synthesis was not investigated.

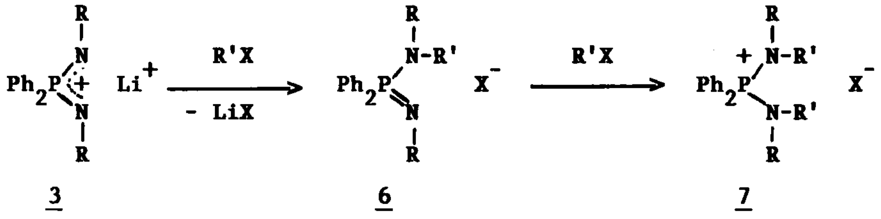
In the case of phosphonium diaza-diylids 3, a general and easy preparation of the reagents was first developped by direct lithiation of diaminodiphenylphosphonium salts 5, an original synthesis of which was obtained by adjusting the Horner's preparation of monoaminophosphonium salts to the *in situ* preformed trihalogenophosphorane :

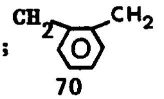


R = nBu $\delta^{31}P$ = 36.5 ppm $\delta^{31}P$ = 11.7 ppm

The synthesis of salts 5, which can be performed in a one-pot procedure, affords good to very good yields (55-85 %). The method is general in regard to the alkyl, aryl or functional nature of the R group and furthermore can be applied to heteroatomic substituents (R = NH-Ph for example).

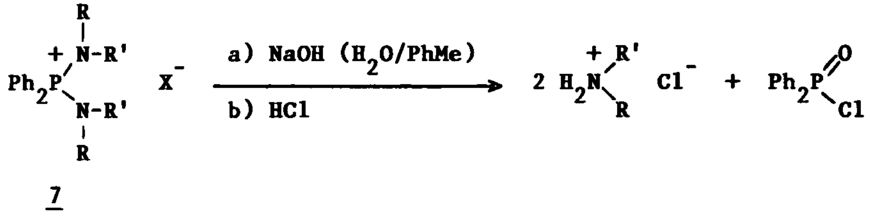
The diaza-diylids 3 react with various alkylating agents (among them tosylates appear to be generally the most effective), to afford alkylated diaminophosphonium salds. Depending on the solvent, temperature and time of the reaction, the mono- and dialkylation process can be fully controlled and give very high yields (80-95 %) in the corresponding products 6 or 7.



7 R = nBu ; R' =	CH_2=CH-CH_2 ;	CH_3-CH=CH-CH_2 ;	CH=CH_2 ;	
(%)	79	64	46	70

The alkylation can take place with a normal alkyl group, but the reaction is easier with an allylic, benzylic or α-functional R'X moiety. The salts 7 can also have a cyclic structure in the case of divalent alkylating agent (X-R"-X).

Hydrolysis of diaminophosphonium salts 7 occurs in two steps : the first P-N cleavage takes place easily with aqueous NaOH and the second one, in the phosphonamide structure, by usual anhydrous HCl treatment. The two steps can be performed one-pot (using toluene as solvent for intermediate azeotropic water-distillation) and affords excellent overall yields (90-95 %) in secondary amines hydrochlorides.



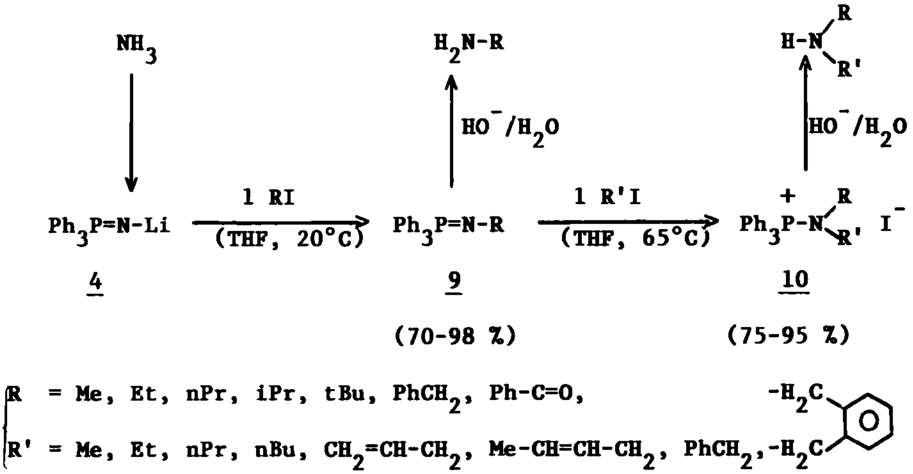
In the case of the aza-yldiid 4, we developped a new synthesis of this reagent by bis-deprotonation of the corresponding aminophosphonium salt 8 obtained directly from ammonia :

$$Ph_3P \xrightarrow[b)\ NH_3\ g.]{a)\ Br_2(CH_2Cl_2)} Ph_3\overset{+}{P}{-}NH_2\ \ Cl^- \xrightarrow[-\ LiCl]{2\ nBuLi} Ph_3P{=}N{-}Li$$

8

$\delta^{31}P = 35.5$ ppm $\qquad \delta^{31}P = -\ 11$ ppm

The stepwise dialkylation of reagent 4 can be controlled and give very good yields (70-95 %) of N-alkyl (or N-acyl) phosphinimines 9 or disubstituted aminophosphonium salts 10, hydrolysis of which affords respectively the corresponding primary amines (or amides) and secondary amines.



R = Me, Et, nPr, iPr, tBu, $PhCH_2$, Ph-C=O,

R' = Me, Et, nPr, nBu, CH_2=CH-CH_2, Me-CH=CH-CH_2, $PhCH_2$, $-H_2C$…$C H_2-$

In conclusion, the diaza-diylids 3 or aza-yldiid 4 are simple and efficient reagents for primary and secondary amine synthesis, which display complementary characteristics in regard to other phosphorus aminating agents already described in the literature[10,11]. Indeed, our reagents exhibit :

- high nucleophilicity toward alkylating agents (as well as toward other electrophilic substrates), owing to the double negative charge α to phosphorus
- a good ability for the synthesis of cyclic amines or diamines thanks to favourable entropic factors.

They also open two further possibilities : a) to modulate the reactivity by changing the associated cations (transition metals can be used in state of lithium) ; b) to perform asymetric synthesis using a chiral phosphorus part. These possibilities are now under investigation, together with the aza-Wittig reactions of reagents 3 and 4.

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