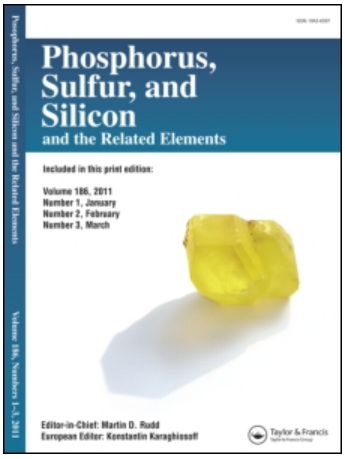

Phosphorus, Sulfur, and Silicon and the Related Elements

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New Synthetic Applications of Metallated Ylids

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NEW SYNTHETIC APPLICATIONS OF METALLATED YLIDS

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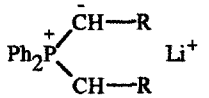
Abstract The reaction of diylids 1 toward carbonates, carbamates, thiocarbamates, isocyanates, carbodiimides and sulfinates allow the quantitative preparation of functional Wittig reagents, which can be used *in situ* in the E-stereoselective synthesis of the corresponding α,β-unsaturated derivatives of carboxylic (or sulfinic) acids. The diylids 2 or yldiid 3 can be used as synthetic equivalents of RNH_2^- or NH^{2-} anions and allow normal or functional alkylation of the nitrogen atom.

Since 1987, we are investigating metallated ylids[1-3] : diylids 1, 2[1,2] (issued from dialkyl[1] or diamino[2] phosphonium salts) and yldiid 3[2b,3] corresponding to the metallated phosphinimine. Our first results showing the potential synthetic interest of diylids, owing to their strong nucleophilicity, were followed by Walker's[4] and Mioskowski's[5] investigations on the stereochemistry of the Wittig reaction with aldehydes and ketones.



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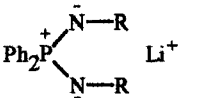

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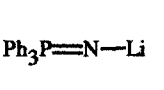

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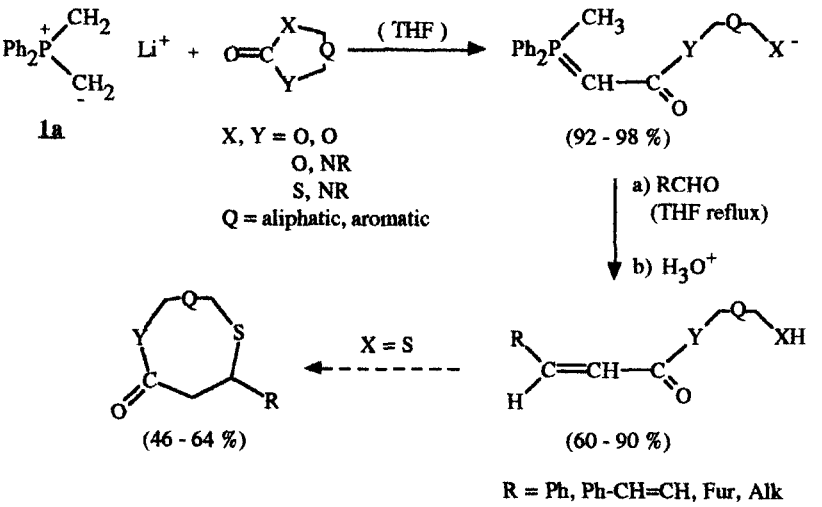
Concerning diylids 1, we have developped[6] an efficient preparation of dialkyl-phosphonium salts with different groups R and we have already published different synthetic results about reactions of diylids 1 towards overcrowded ketones[1b], and esters or amides[1a,c].

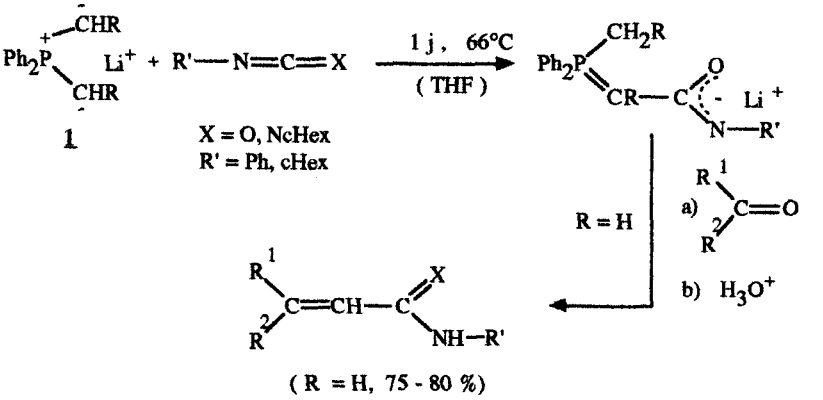
Herein, we present new investigations about reactivity of diylids 1 towards weakly electrophilic carbonyl compounds derived from carbonic acid and carbonic anhydride, or towards sulfur compounds.

Diylid 1a readily attacks cyclic carbonates, carbamates and thiocarbamates, resulting quantitavely in "pseudo-acylation" products. The new stabilized ylids thus obtained can be used *in situ* as carbonylolefination reagents

towards aldehydes. This procedure is a new one pot method for the synthesis of E-vinylic esters and amides, bearing a free ω-alkohol or ω-thiol group (the later can give intramolecularly a pseudo-Michael reaction to afford a sulfur heterocycle).

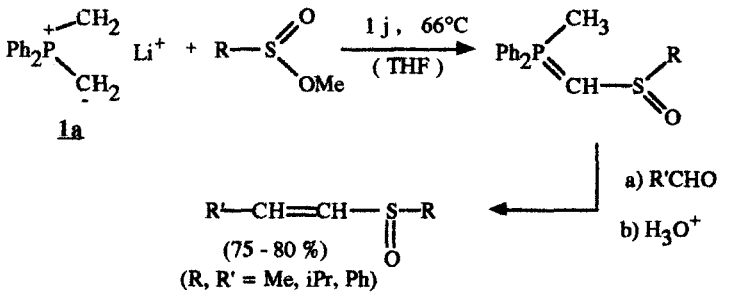


Differently substituted diylids 1 react with phenylisocyanate and carbodiimides in a pseudo-acylation way to yield metallated monoylides. The corresponding phosphonium salts can be isolated in high yields by acidic work-up. But their use *in situ* also allows Wittig reaction with aldehydes and ketones : that is an efficient route to α,β-unsaturated anilides and amides with high E-stereoselectivity (R^1 = H : E/Z > 99/1).

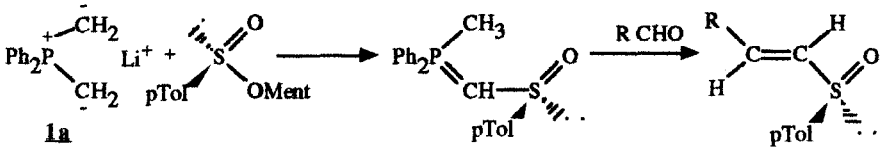


Then we studied the reactivity of diylids towards different sulfur compounds tri- or tetracoordinated bearing (or not) a leaving group : sulfoxides, sulfones, sulfinates and sulfates. In the case of sulfinates, an easy sulfination reaction

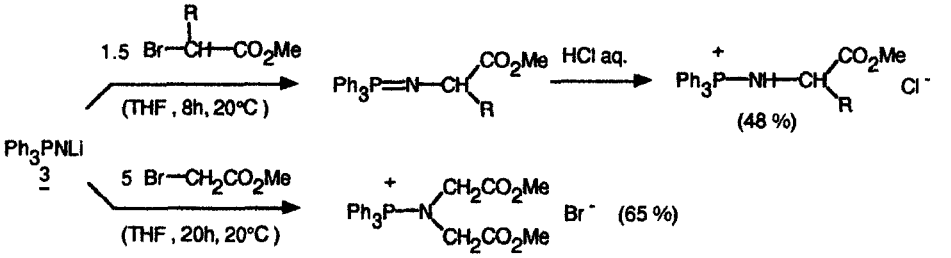
takes place and affords a new one-pot synthesis of vinylsulfoxides starting from aryl or alkylsulfinates, with an excellent stereoselectivity (E/Z > 91/9).



The same reaction with a chiral sulfinate leads to the chiral E-vinylsulfoxides (E/Z > 99/1), with an inversion of configuration at the sulfur atom higher than 96 %.

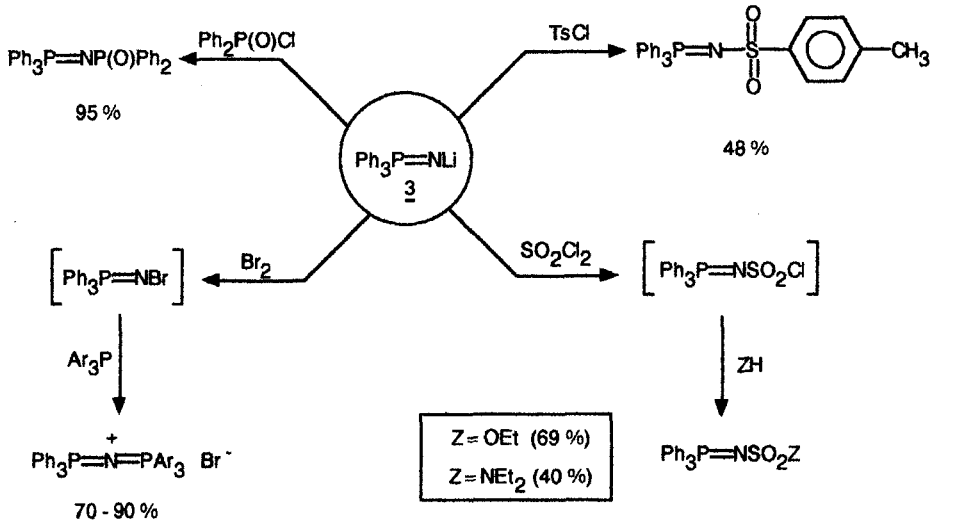


Concerning diazadiylids **2** or azayldiid **3**, as shown in our previous works[2,3], they are synthetic equivalents respectively for the synthons RNH^- and NH^{2-} and they can be easily selectively mono- or dialkylated before deprotection.
With diazadiylids **2** we are developping new applications for the synthesis of polyamines of biological interest (spermine, spermidines...) using cyclic diaminophosphonium salts.
Concerning the reagent **3** we have investigated its reactivity towards other electrophilic substrates. In the field of functional alkylation, our results with α-bromoesters afford a preparative way to aminoacids.



With phosphorus or sulfur electrophilic substrates, the reagent **3** affords an easy *one-pot* preparation for a large range of N-substituted phosphonimines,

which are valuable precursors for the (poly-) phosphazene or sulfonamide chemistries.



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