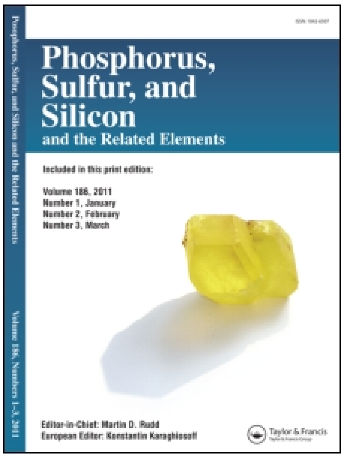

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Taillefer, Marc , Cristau, Henri-Jean , Jouanin, Isabelle , Inguimbert, Nicolas and Jäger, Lothar(1999) 'Phosphonium Diylides in Organic Synthesis', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 401 — 404

To link to this Article: DOI: 10.1080/10426509908546266

URL: http://dx.doi.org/10.1080/10426509908546266

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 401-404
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Phosphonium Diylides in Organic Synthesis

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Phosphonium diylides afford a general synthetic method for numerous α,β-unsaturated functions, the double bond being di- or trisubstituted. The diamino-phosphonium diylides, obtained in the case of stabilized ones by a new variation of the Staudinger reaction, are also interesting tools in synthesis because they allow access to, for example ketenimines, phosphorus guanidines or triazaphosphinimines.

Keywords: phosphonium diylides; Staudinger Reaction; cetenimines; phosphorus guanidines; triazaphosphinimines; α,β-unsaturated functions

INTRODUCTION

As part of the study of the reactivity of lithium phosphonium diylides **1**[1], we have developed a general synthetic way to these reagents, involving the metallation of the corresponding phosphonium salts. Diylides **1**, until recently mainly used in coordination chemistry[2], find in fact numerous applications in organic synthesis[3a]. Therefore, we have also developed a convenient method of preparing their nitrogen analogues, the diaminophosphonium diylides **2**, in order to exploit their synthetic potential.

1

R = H, alkyl, phenyl, C(O)R'...

2

R = alkyl, aryl, electronwithdrawing group / M = Li, Na

FIGURE 1. Phosphonium diylides **1**, and their nitrogen analogs **2**.

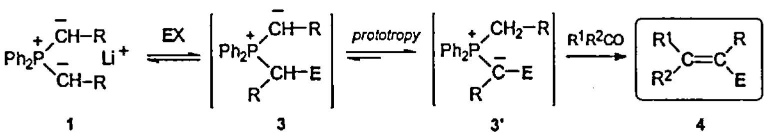
We present here an overview of the synthesis, reactivity and applications of phosphonium diylides **1**, and of their nitrogen analogues **2**.

RESULTS AND DISCUSSION

Diphenylphosphonium diylides.

Synthesis: Phosphonium diylides type **1** are obtained by the addition of two base equivalents to the corresponding phosphonium salts. For the preparation of the latter, we have develop a general one-pot procedure, involving the double alkylation of lithium diphenylphosphide, itself generated from triphenylphosphine. This method allows the synthesis of all type of diylides regardless of their non-stabilized (R = H, alkyl), semi-stabilized (R = aryl) or stabilized (R = electronwithdrawing group) character.

Reactivity and applications: The scheme below shows that phosphonium diylides **1** can react with electrophiles (EX) to give the corresponding intermediate monoylides **3**. The latter, through an intramolecular prototropy, are transformed into new functionalized monoylides **3'** able to react *in situ* with aldehydes or ketones to give α,β–unsaturated functions, the double bond being, depending on the case, di- tri- or tetrasubstituted.



SCHEME 1. Reaction of **1** with electrophiles EX, followed by a Wittig reaction

Thus, starting from non stabilized phosphonium diylides **1a** (R = H, alkyl) we could develop the *E* stereoselective synthesis of α,β–unsaturated amides[3b] (**A** : EX = PhNCO), amidines[3b] (**B** : EX = $C_6H_{12}NCNC_6H_{12}$), esters or acids[3c] (**C** : EX = $(RO)_2CO$) or vinylic sulfoxides[3d] (**D** : EX = RSO_2Me). In the same way, the *Z* stereoselective synthesis of α,β–unsaturated phosphines and of butadienic phosphines could also be achieve (**E** : EX = Ph_2PCl). These reactions are usually performed in mild conditions in presence of aldehydes (R_1R_2CO = PhCHO, 5 minutes at room temperature), more drastic conditions being required in the case of ketones (several hours at 60°C).

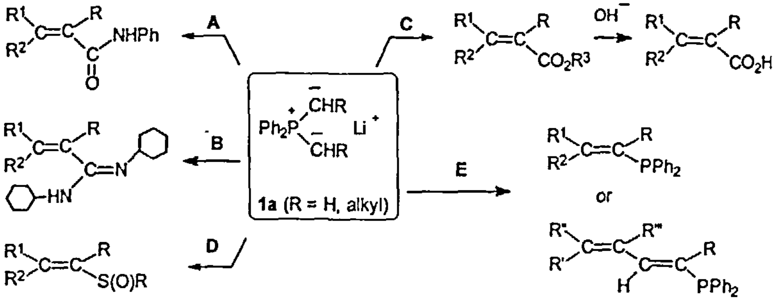
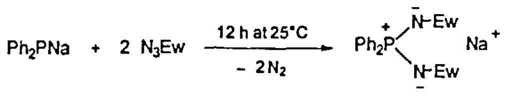


FIGURE 2. Synthesis of α,β-unsaturated functions from diylides **1a**.

The stabilized diylides **1c** (R = electronwithdrawing groups) are usually weakly reactive towards electrophiles. The intermediate category, the semi-stabilized diylides **1b** (R = aryl), react with electrophiles but lead often to the olefination products resulting from a Wittig reaction between the carbonyl compounds and the intermediate monoylides type **3**.

Diphenyldiaminophosphonium diylides.

Synthesis: non stabilized (**2a** ; R = alkyl) and semi-stabilized (**2b** ; R = aryl) diylides type **2** are easily synthesized by the direct dilithiation of the corresponding diaminophosphonium salts, themselves obtained *via* the addition of two equivalents of amines on a trihalogenophosphorane. This being an inefficient way of preparing the stabilized diaminophosphonium diylides (**2c** ; R = electronwithdrawing group), we have developed for them an original synthesis, involving the reaction of sodium diphenylphosphide with azides. This new variation of the Staudinger reaction permit us to obtain the first known examples of this type of diylide.

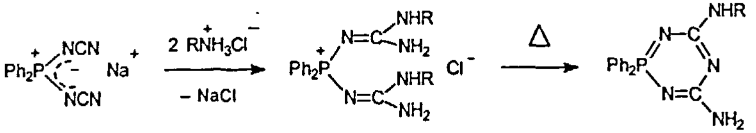


$$Ph_2PNa + 2\ N_3Ew \xrightarrow[-\ 2N_2]{12\,h\ at\ 25^\circ C} Ph_2\overset{+}{P}\left(\overset{-}{N}\text{-}Ew\right)\left(\underset{-}{N}\text{-}Ew\right)\ Na^+$$

2c Ew = CN, COAr, $SO_2C_6H_4CH_3$

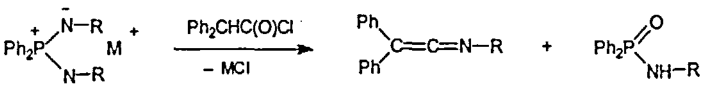
Reactivity and applications: Stabilized diphenyldicyanamidophosphonium diylide type **2c** (Ew = CN), in presence of ammonium chloride, lead to the formation of bis(guanidino)phosphonium salts, which are molecules of agrochemical interest. The generalization of this method to other cyanamidophosphonium ylides, has permitted us to develop a convenient and general access to other types of phosphorus guanidines[4].

Notice that by heating the bis(guanidino)phosphonium salts, we could quantitatively obtain heterocyclic compounds, the triazaphosphinimines, also interesting in agrochemistry.



2c (R = CN) *bis(guanidino)phosphonium salts* *triazaphosphinimines*

The reaction of diylides, regardless of their degree of stabilization, with diphenylacetylchloride, can also be applied to the synthesis of various ketenimines.



2a-c M = Li, Na R = alkyl, aryl, COAr

CONCLUSION

Phosphonium diylides **1** and **2** are convenient versatile tools in organic synthesis. Their broad field of application is currently under investigation. At the moment, we are developing the butadienic phosphine synthesis, the product of which can be used as reagent for Diels Alder reactions or as coordination ligands. We also studying the reactivity of diylides **1** together with α,β-unsaturated functions in order to develop new pathways to heterocyclic compounds. Finally, we want to develop from stabilized diylides **2c** (R = CN) the synthesis of biguanidines and of triazaphosphinimines bearing amino acids substituents, these molecules being of interest in the field of medicine.

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