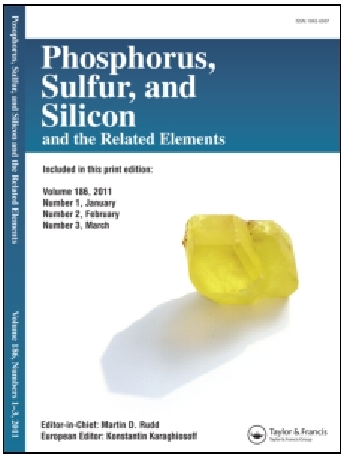

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Use of Phosphonium Diylids in Organic Synthesis

Henri-Jean Cristau[a]; Yves Ribeill[a]; Francoise Plenat[a]; Laurent Chiche[a]
[a] Laboratoire de Synthèse Organique ENSCM (Unité Associée au CNRS n° 458, Institut de Chimie Fine), MONTPELLIER CEDEX

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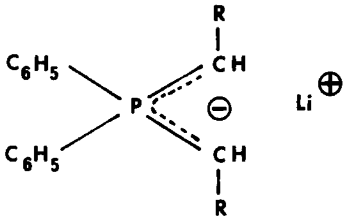
USE OF PHOSPHONIUM DIYLIDS IN ORGANIC SYNTHESIS.

HENRI-JEAN CRISTAU*, YVES RIBEILL, FRANCOISE PLENAT et
LAURENT CHICHE.
Laboratoire de Synthèse Organique ENSCM (Unité Associée
au CNRS n° 458, Institut de Chimie Fine), 8 rue de l'Ecole
Normale 34075 MONTPELLIER CEDEX.

Abstract Reactivity of phosphonium diylids towards such carbonyl compounds as ketones, esters, carbonates, amides... has been investigated. The Wittig reaction was obtained with some amides.

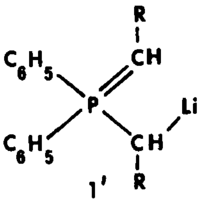
Since the classical work of H. Schmidbaur[1], phosphonium diylids such as 1 are well known compounds used mainly as ligands for metal coordination chemistry; but, till now, their use as reagent for organic synthesis has been very scarcely investigated[2 3].



1

a : $R = H$; a' : $R = C_2H_5$
b : $R = C_6H_5$; b' : $R = CH{=}C(CH_3)_2$
c : $R = COC_6H_5$

Nevertheless, the structure of such compounds can be compared, in their mesomeric form 1', to the phosphonium monoylid 2 or α-phosphoryl carbanions 3, 4 corresponding to the usual Wittig and Wittig-Horner reagents. The comparison lets us expect interesting application in organic synthesis thanks to a higher nucleophilic reactivity, a double nucleophilic character and the possibility to change the electrophilic character of phosphorus during the course of the reaction.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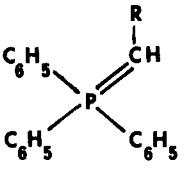
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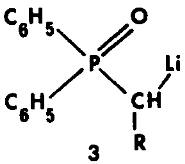
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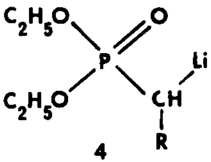
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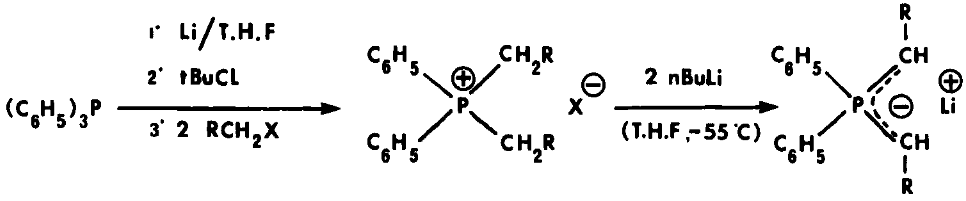
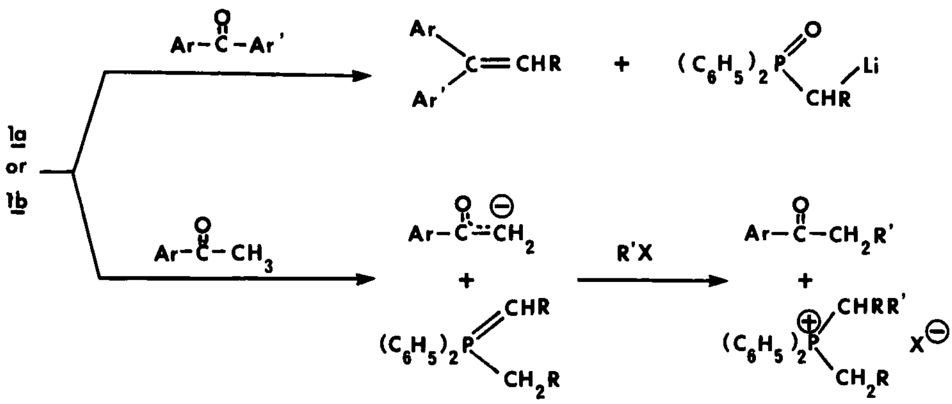
We have prepared, in a classical way[1], non stabilized (1a, 1a') semi-stabilized (1b, 1b') and stabilized (1c) diylids with a view to investigate their reactions toward various electrophilic substrates.

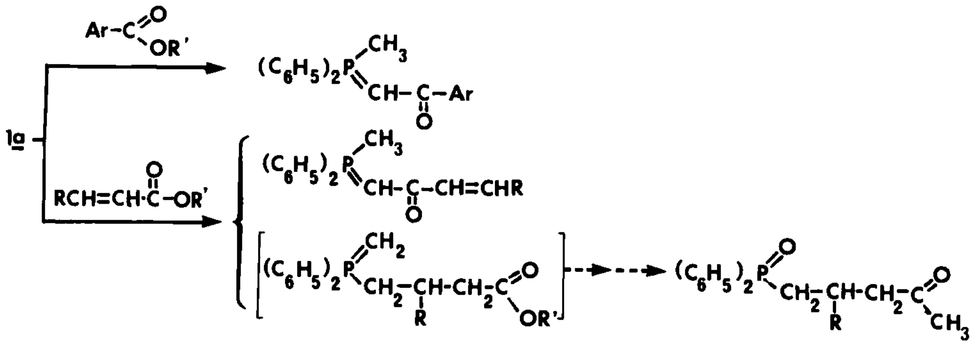


The olefination of aldehydes with diylid 1 and with the corresponding 2 and 3 reagents sets good examples for the higher reactivity of the diylid (higher speed, lower temperature and better yields).

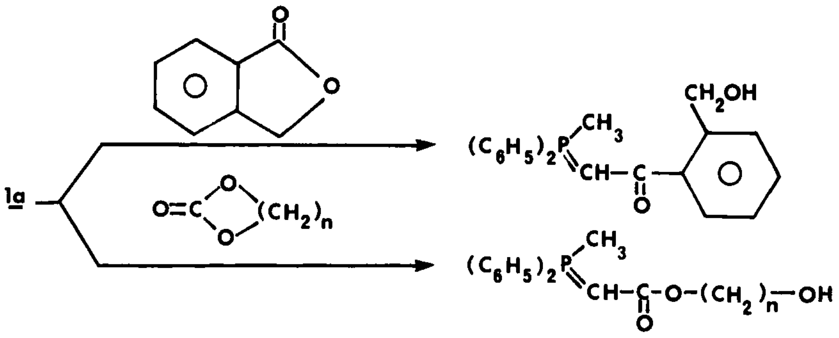
Moreover, the reaction of diylid 1a and 1b with ketones shows a sharp difference with the corresponding Wittig's phosphonium monoylid : with non enolizable ketones the expected reactions take place more easily but, furthermore, with enolizable ketones, these diylids do not give the direct olefination but enolization :



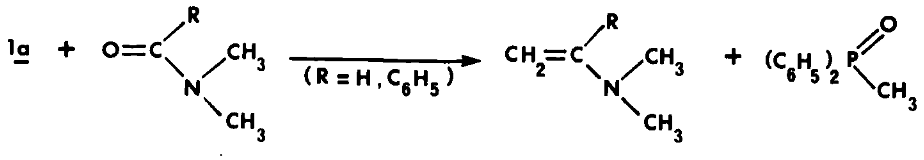
The higher basicity of diylids is strenghtened by their reactions with esters : aromatic esters react at -55°C, mainly as acylating agents, but aliphatic esters undergo enolization, and furthermore α,β -unsaturated esters give noteworthy 1,4 additions parallel to acylations.



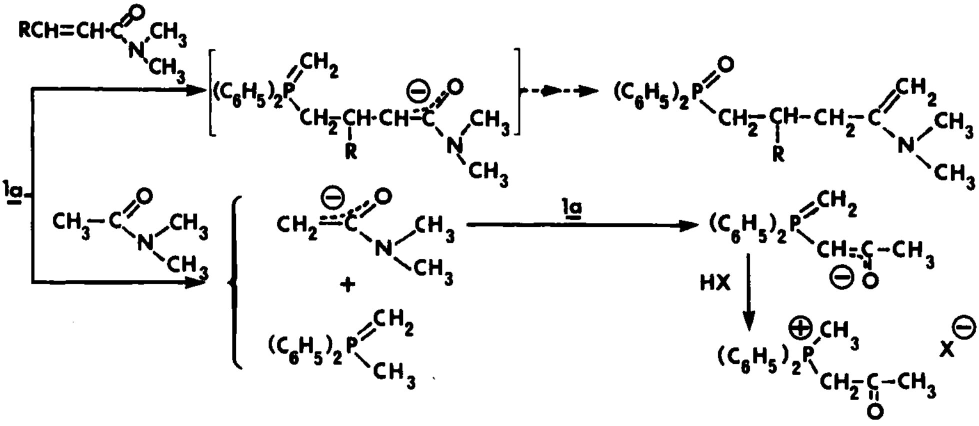
The acylation reaction is also encountered with non enolizable lactones and with cyclic carbonates, in spite of unfavorable entropic effects for the cleavage of the alkoxy leaving groups. In all cases it is noteworthy that the reaction takes place easily at -55°C.



With aromatic amides or formamides the reaction of non stabilized diylid 1a is particularly interesting because it can be controlled to give good yields of enamines which can be trapped, for example by alkylating agents, or hydrolysed to the corresponding ketones.



α,β-unsaturated amides, like α,β-unsaturated esters, give mainly 1,4-addition prior to olefination. With aliphatic amides the equimolecular reaction takes place with enolization but an excess of diylid allows the enolate to react at last, giving the acylation product.



Attempts to let react amides with till lower electrophilic reactivity, afford poor results in olefination in spite of a long reflux period : cafeine (17%), urea (10%).

As expected we have found marked differences between the three kinds of diylids 1, with a much higher reactivity of the non stabilized one 1a, 1a'. For example, the semi-stabilized diylid 1b react in the same way as 1a with aromatic esters, but only at 20°C ; and it does not react with less electrophilic aromatic amides, even after one week reflux.

In conclusion our first results on the reactivity of phosphonium diylid toward various electrophilic organic substrates show a high nucleophilic reactivity, which allow reactions with compounds, such as esters and amides, normally unreactive toward Wittig's monoylids.

Our study is till in progress, particularly by varying the organic substrates (nitriles, isocyanates ....)and by changing the nature of the coordinated metal.

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