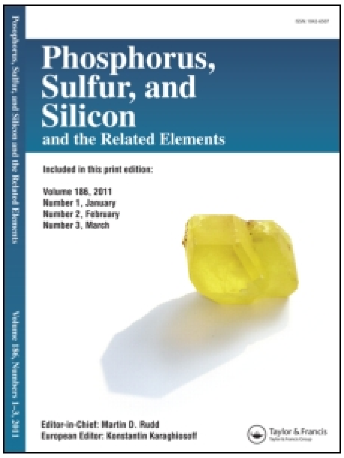

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Attempts to Rationalize the Chemical Reactivity of the 1-3 Dipolar Species Obtained when a Phosphite Reacts with Activated Ethylenic or Acetylenic Ketones or Esters

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To cite this Article Leroux, Yves , Manouni, Driss El , Jaafar, Brahim Ben and Burgada, Ramon(1983) 'Attempts to Rationalize the Chemical Reactivity of the 1-3 Dipolar Species Obtained when a Phosphite Reacts with Activated Ethylenic or Acetylenic Ketones or Esters', Phosphorus, Sulfur, and Silicon and the Related Elements, 18: 1, 205 — 208

To link to this Article: DOI: 10.1080/03086648308076002

URL: http://dx.doi.org/10.1080/03086648308076002

Phosphorus and Sulfur, 1983, Vol. 18 pp. 205-208
0308-664X/83/1801-0205/$18.50/0

ATTEMPTS TO RATIONALIZE THE CHEMICAL REACTIVITY OF THE 1-3 DIPOLAR SPECIES OBTAINED WHEN A PHOSPHITE REACTS WITH ACTIVATED ETHYLENIC OR ACETYLENIC KETONES OR ESTERS

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Abstract - Addition of trivalent phosphorus compounds with α,β ethylenic ketones and esters leads to examples of prototropy or cyclisation or rearrangement with ring expansion from 5 to 7 atoms.

When trivalent phosphorus compounds react with acetylenic ketones and esters, the 1,3 dipolar species can be trapped with an electrophilic reagent (aldehydes or the original acetylenic compound) or a protic reagent (alcohol, acid,amide, phenol, etc...) Ylides, phosphoranes, spirophosphoranes and phospholes can be obtained.

The reactions of trivalent phosphorus compounds with diunsaturated compounds such as ethylenic ketones, dienes etc... have been widely studied. These reactions are known to give either phosphoranes, ylids or phosphonium salts[1]. In this work, we planned a study of the various kind of factors able to modify the course of the reaction which lead to the postulated intermediates. The results presented in this paper deal with the following strategy :

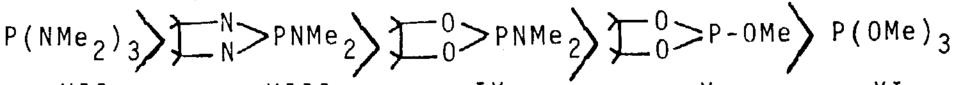
1°/ Choice of the tricoordinated species based on such properties as its : nucleophilicity, stereochemistry, position on the hard and soft scale, etc... and choice of the unsaturated compound with regard to the same factors.

2°/ Trapping of the intermediates by a proton transfer or by the addition of a new reagent[2].

It was found that the ionic 1,3 dipolar species possesses two methods of stabilization : either by prototropy giving an ylid or through an enolate structure giving a phosphorane. Five triply connected phosphorus compounds were tested with these substrates.

In order to rationalize the experimental results, the factors can be considered :

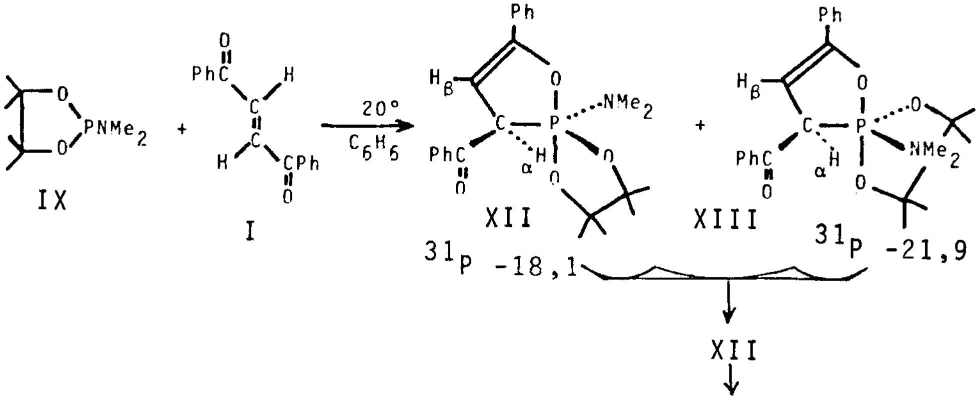
- Reactivity : the order is



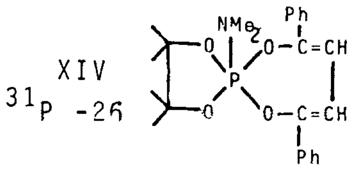
VII VIII IX X XI

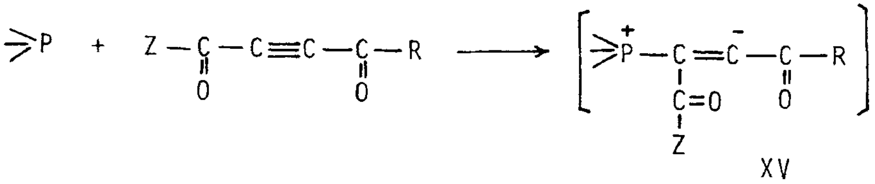
- Orientation : Addition is 1,4 on the more reactive system.
- HSAB theory favors ylid formation with a very soft acid (i.e $\overset{+}{-}P(NMe_2)_3$) and a very soft base (i.e ester enolate).

On the other hand, phosphorane formation is encouraged with an hard-hard interaction and with cyclic tricoordinated reagents. We observe a rearrangement reaction : Trans dibenzoylethylene I with cyclic phosphite IX gives exclusively two pentacoordinated species XII and XIII. These species are diastereoisomers because of the presence of two chiral centers phosphorus and carbon in the molecule. The isolation of XII and XIII is not possible. XIII isomerises to XII which in turn disappears and a new spirophosphorane XIV is formed. XIV is stable and can be isolated. The conversion of XII and XIII to XIV is quantitative and demonstrates a new rearrangement reaction with ring expansion (5 to 7 atoms) This ring expansion implies that a P-C bond is broken in the transition state.

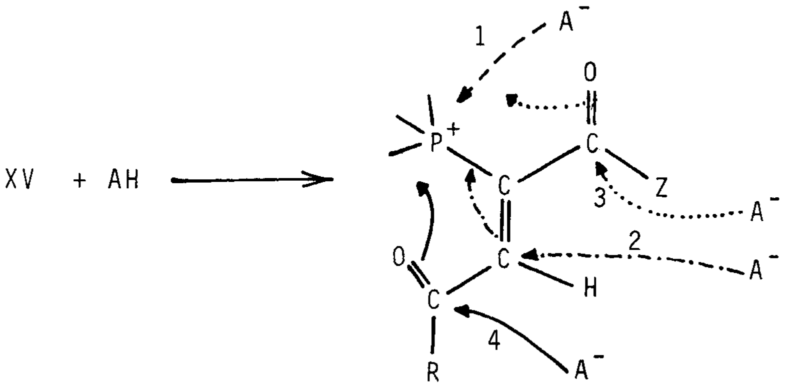


With activated acetylenic ketones or esters, the general scheme is :





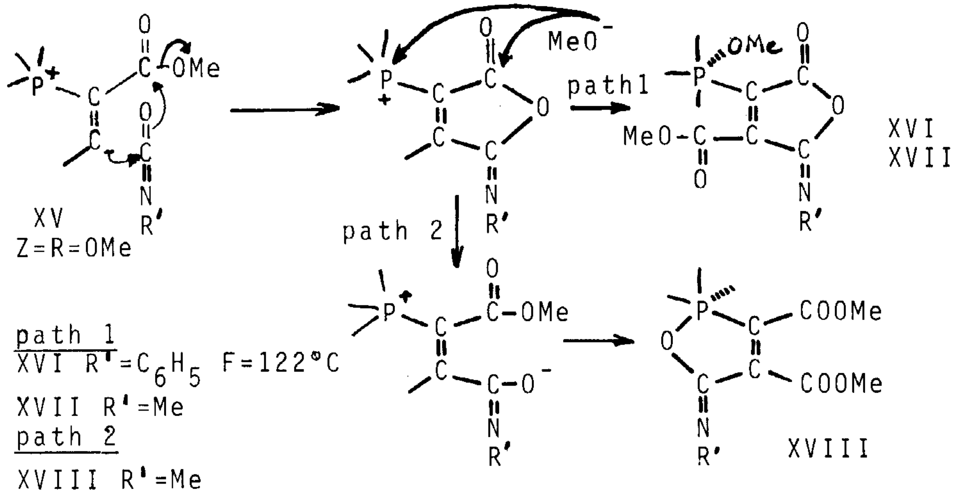
The dipolar species XV can be trapped with various electrophiles[3] (protic or aprotic) :



path 1: vinylic phosphorane
path 2: ylid
path 3: cyclic phosphorane(4m^{d} ring)never observed
path 4: cyclic phosphorane(5m^{d} ring)allways observed

Addition process on the triple bond : stereochemistry. Nucleophilic addition is already known to be trans.

With methyl isocyanate which is much more reactive than phenyl isocyanate, the reaction must be performed at -50°C and two phosphoranes are trapped.



XV
Z=R=OMe

XVI
XVII

XVIII

path 1
XVI R'=C_6H_5 F=122°C
XVII R'=Me
path 2
XVIII R'=Me

These two examples provide evidence that the addition to the triple bond is trans leading to the kinetic product XVII which can then rearrange to give the thermodynamic product XVIII. In the case of XVI, it is both the thermodynamic and kinetic product.

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