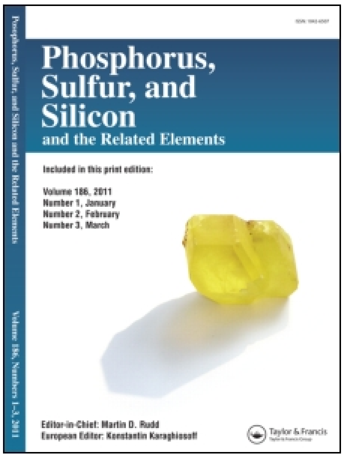

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THE CARBENIC INSERTION INTO THE P-P BOND

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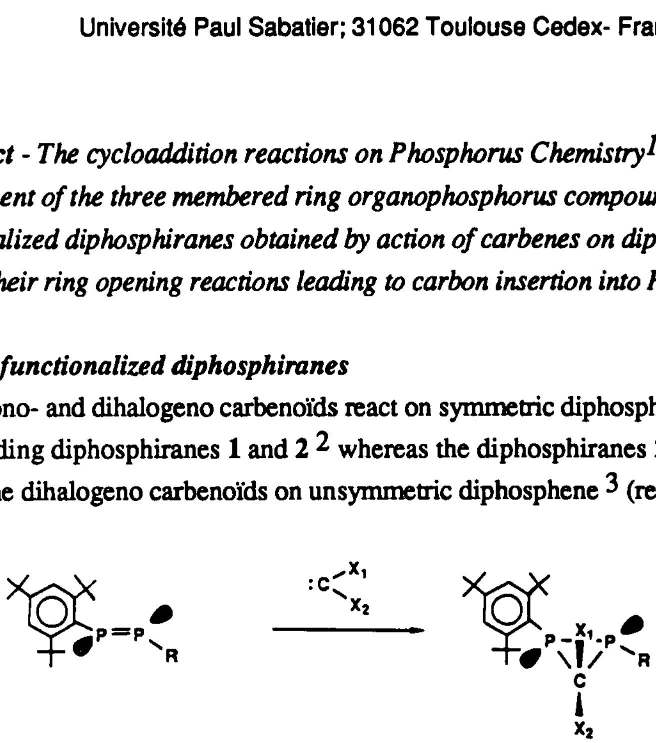
***Abstract** - The cycloaddition reactions on Phosphorus Chemistry[1] has allowed a new development of the three membered ring organophosphorus compounds. Starting from functionalized diphosphiranes obtained by action of carbenes on diphosphenes, we have studied their ring opening reactions leading to carbon insertion into P-P bond.*

1- The functionalized diphosphiranes

The mono- and dihalogeno carbenoïds react on symmetric diphosphene leading to the corresponding diphosphiranes **1** and **2** [2] whereas the diphosphiranes **2'** are obtained by action of the dihalogeno carbenoïds on unsymmetric diphosphene [3] (reaction A).



Reaction A

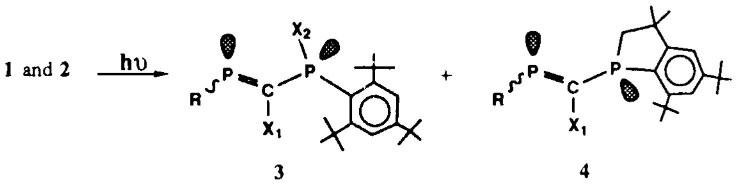
1 : R= Ar X_1=Me,Ph X_2 =Cl,Br
2 : R= Ar X_1=X_2=Cl,Br
2': R= $C(SiMe_3)_3$ X_1=X_2=Cl,Br

The X-ray structure of **2** (X_1=X_2= Cl)[4] confirms the stereoselectivity of the cyclopropanation reaction and is consistent with the perpendicular approach of the carbene to the symmetric plane of starting diphosphene.The intracyclic P-P and P-C bond lengths are 2.245 Å and 1.863 Å whereas the PCP and PPC angles are 74.3° and 52.7°.

The presence of good leaving group on the intracyclic carbon and the fact that the P-P bond is weaker than the P-C bond, induce in all cases, preferential intracyclic P-P bond rupture leading to the ring opening reactions.

2- Photochemical ring opening

All the functionalized diphosphiranes irradiated (under 250 or 300 nm) in degazed solvents, lead to diphosphapropenes **3** and **4** (reaction B).



Reaction B

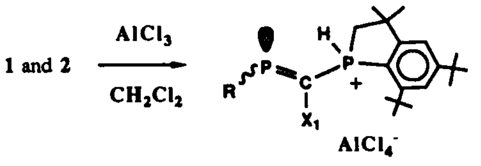
The major product **3** (about 80 %), functionalized diphosphapropene obtained after the P-P bond rupture and halogen migration from the carbon to the phosphorus atom is a mixture of cis and trans isomers (10/90) with different ^{31}P NMR parameters.The trans configuration of the 1,3-diphosphapropene **3** (X_1=X_2=Cl) is confirmed by an X-ray diffraction study [4].

The minor product **4** (10%) is a diphosphapropene in which the deshydrohalogenation induces the classical rearrangement of the tBu group of the phosphorus substituent.

By ESR, using the spin trap method, the diphosphiranyl and diphosphapropenyl intermediates were characterized.

3- Cationic ring opening reactions

The action of the Lewis acids on the mono- and dihalogenated diphosphiranes **1** and **2** induces the ring opening.The cyclic diphosphiranium and the diphosphaallyl cations are not detected but we isolated the phosphonium phosphaalkenes **5** [5](reaction C).

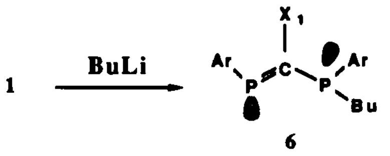


5

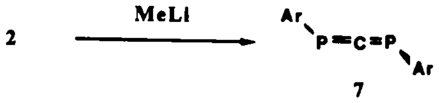
Reaction C

4- Anionic ring opening reactions

The diphosphiranes **1** react with an excess of alkyl lithium at low temperature and lead after the ring opening to 1,3-diphosphapropenes **6** (reaction D) whereas the dihalogenated diphosphiranes **2**, under the same conditions, lead to the 1,3-diphosphaallene **7** (reaction E) [6].



Reaction D

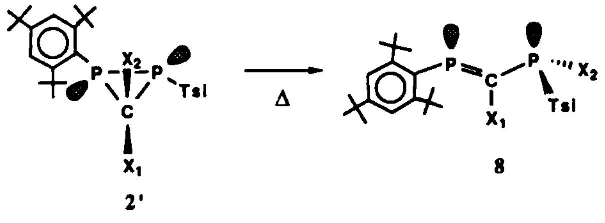


Reaction E

Unlike the cyanocyclopropyl anion [7], the diphosphiranyl anion intermediate is not detectable,but the intermediate 1,3-diphosphaallyl anion is observed only the for monohalogenated diphosphiranes **1** when the progress of the reaction is followed by ^{31}P NMR at low temperature [8].

5- Thermal ring opening

The unsymmetric diphosphiranes **2'**, less stable than their symmetrical homologues undergo thermal ring opening and lead to the 1,3-diphosphapropenes **8** (reaction F).



Reaction F

The NMR parameters of the functionalized diphosphapropenes **8** are very different to their homologues **5**.

The X-ray analysis indicates that **8** (X_1=X_2=Cl) in a trans configuration[3] has a particular conformation in which the two phosphorus lone pairs are nearly in the same (PCP) plane (Figure 1).The aryl group is perpendicular (89°) to the P(2)-C(2)-P(1) plane containing the double bond. The dihedral angle between the two planes (P(2)-C(2)-Cl(2)) and (Cl(2)-C(2)-P(1)) is 12°, so the P(1) phosphorus lone pair nearly eclipses the C=P double bond. The syn position of the two phosphorus lone pairs can explain the $^{2}J_{PP}$ coupling constant enhancement.

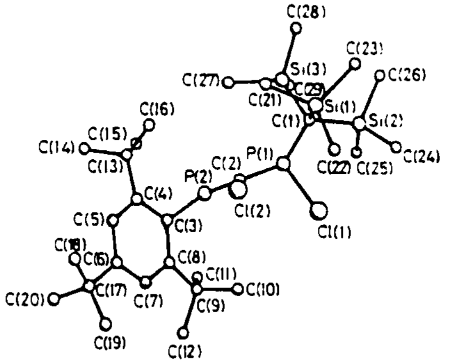


Figure 1- X-ray diffraction structure of 1,3-diphosphapropene **8**. Important bond lengths (A) and angles (°): P(1)-C(2) 1.835(7), C(2)-P(2) 1.670(8), Cl(1)-P(1) 2.095(3), C(2)-Cl(2) 1.741(7); P(2)-C(2)-P(1) 110.3(4), C(3)-P(2)-C(2) 104.7(3), C(2)-P(1)-C(1) 117.0(3); torsional angles(°): Cl(2)-C(2)-P(1)-C(1) 54(2), Cl(2)-C(2)-P(1)-Cl(1) 54(2), C(3)-P(2)-C(2)-P(1) 168(2).

The formation of functionalized diphosphiranes induces a skeletal disymmetry and constitutes an appropriate pattern for the experimental and theoretical approach of the electrocyclic reactions, which are well described in the chemistry of the cyclopropanes but not in heteroelementar chemistry and in particular in phosphorus chemistry.

The study of the reactivity of these strained models under irradiation, or heating, as well as the action of organoalkali metals,and Lewis acids lead invariably to the ring opening reactions.The stereochemistry of the ring opening products can be discussed in term of electrocyclic reactions.

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