Cheletropic Reactions in Diphosphirane Series

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<u>Abstract</u>: In the diphosphirane serie, whereas the fragmentation is a side reaction during the photochemical, thermal or cationic ring opening, the oxidation of the phosphorus lone pairs leads quantitatively to the corresponding phosphaalkenes, and the unstable phosphinidene.

The cheletropic reactions in cyclopropane serie have been largely studied both experimentally and theoretically.¹ In the heterocyclopropane serie, these $[3 \rightarrow 2+1]$ cycloelimination reactions are conveniently used as method of generation of silylenes² or germylenes.³ In phosphirane serie, owing to the difference of C-C and P-C bond enthalpy values (83 and 64 Kcal.mol⁻¹, respectively),⁴ the two P-C bond ruptures have exclusively been observed, and the thermal fragmentation reactions are always accompanied by a necessary stabilization of the liberated carbenoids. This stabilization occurs by dimerisation⁵ or by intramolecular rearrangement.⁶ A similar approach has not been studied in the diphosphirane analogues where the low P-P bond enthalpy value (50 Kcal.mol⁻¹)⁴ must involve ring opening by a preferential P-P bond rupture, avoiding the fragmentation reactions. Here, we present cheletropic reactions of diphosphiranes 2 under various conditions (irradiation, heating, oxidation, towards Lewis acids, etc...).

During the synthesis of diphosphiranes 2a-d from the symmetrical diphosphene 1 by cyclopropanation, whatever is the nature of used carbenoids (diazo derivatives, carbenes or halogenocarbenes), in all cases we have already observed as byproducts the formation of the phosphaalkenes 3a-d (or its derivatives) and the unstable phosphinidene 4, which then rearranges (5-20%).⁷



Thus, in the case of the synthesis of methylene diphosphirane 2d, obtained by addition of the unsaturated carbene on diphosphene, we noted the formation of the phosphacumulene 3d (30%), more stable than the parent diphosphirane.⁸



The formation of 3 can be explained by either the addition of excess of carbenes on phosphorus lone pairs of diphosphirane followed by decomposition of the latter, or the fragmentation of diphosphirane. When an excess of dichlorocarbene (or dibromocarbene) is added on diphosphirane 2b (or diphosphirane 2a), we do not observe the addition of carbene on phosphorus lone pair (as described for triphenylphosphine⁹ and for phosphaalkene¹⁰).



The diphosphirane remains unchanged and in no case, we do not detected the formation of phosphaalkenes. So, the carbene does not react on diphosphirane. Consequently, 3 results from the concerted rupture of P-P and P-C bonds of diphosphiranes according to the cheletropic reaction. We have also observed such ruptures when we have studied the behaviour of the functionalized diphosphiranes 1a under irradiation at 300nm (5-10%),¹¹ towards Lewis acids,¹² or by heating. In these conditions, these fragmentation reactions, related to cheletropic reactions, leading to a variety of substituted phosphaalkenes (minor products) have occured in competition with the electrocyclic ring opening reactions involving the formation of the 1,3-diphosphapropenes as main products. Furthermore, we have checked that the phosphaalkenes do not arise from the 1,3-diphosphapropenes.

In the case of unsymmetrical diphosphiranes 2e-f, whatever the experimental conditions (during the synthesis, under irradiation or heating), we obtained either the diphosphirane 2e-f or the 1,3diphosphapropenes without any fragmentation products.¹³ This absence of cheletropic reactions can be probably due to a more stronger and shorter P-C bonds for 2e (1.783 and 1.803 Å)¹⁴ than for 2a (1.858 Å).¹¹



The oxidation of the lone pair of tricoordinated phosphorus atoms generally induces a stabilization of the molecule. Thus, we have attempted to oxidize the diphosphiranes, very bulky and strained phosphines, by different reagents. The sulfuration of diphosphirane 2 does not occured in toluene at reflux.

Ozone being a more suitable reagent for oxidizing the bulky phosphines, 15 the ozonation of diphosphiranes 2 was carried out in dichloromethane at low temperature (-78°C). The completion of the reaction was followed by ^{31}P NMR spectroscopy. We observe the instantaneous oxidation of the phosphorus atom lone pairs with formation of the oxidized product 5, which decomposes at room temperature to phosphaalkene oxide 6, and phosphinic and phosphonic acids. Consequently, the oxidation of the phosphorus lone pairs does not stabilize these strained heterocycles but allows the obtention of the phosphaalkene oxides not readily available by other methods. 16



The reaction of bromine (2 equivalents) with 2b in dichloromethane at room temperature also involved the fragmentation of the heterocycle leading quantitatively to phosphaalkene 3b and dibromophosphine.



Based on semiempirical calculations, the first bands of the photoelectron spectra (PES) of the phosphorus-containing three-membered ring systems could be assigned to linear combinations of the phosphorus lone pairs and the Walsh-orbitals, and due to the low symmetry of the compounds, a strong mixing of lone pairs and Walsh-orbitals was predicted. ¹⁷ In the recent work of Pfister and coll., ¹⁸ the HOMO of the diphosphirane was assigned to the symmetrical combination of the phosphorus lone pairs which is strongly coupled with the σ_{p-p} orbital.

Furthermore, the X-ray structure of diphosphirane indicates the same dihedral angles RPPR for

the starting diphosphene than for the diphosphirane.¹¹ The orthogonality of the two planes (C-P-P-C and diphosphirane ring is probably the consequence of the non-localization of the lone pairs in the sp³ hybridization. So, the oxidation reactions destabilize the cyclic form by weakening both the P-P and P-C bonds, and promote the cheletropic reactions.

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