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1,2,5-Azadiphospholium and 1,3-Diphospholium Ions

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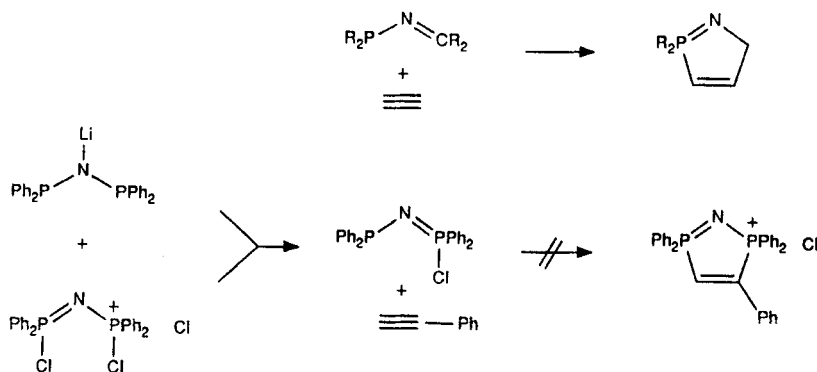
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1, 2, 5-AZADIPHOSPHOLIUM AND 1, 3-DIPHOSPHOLIUM IONS

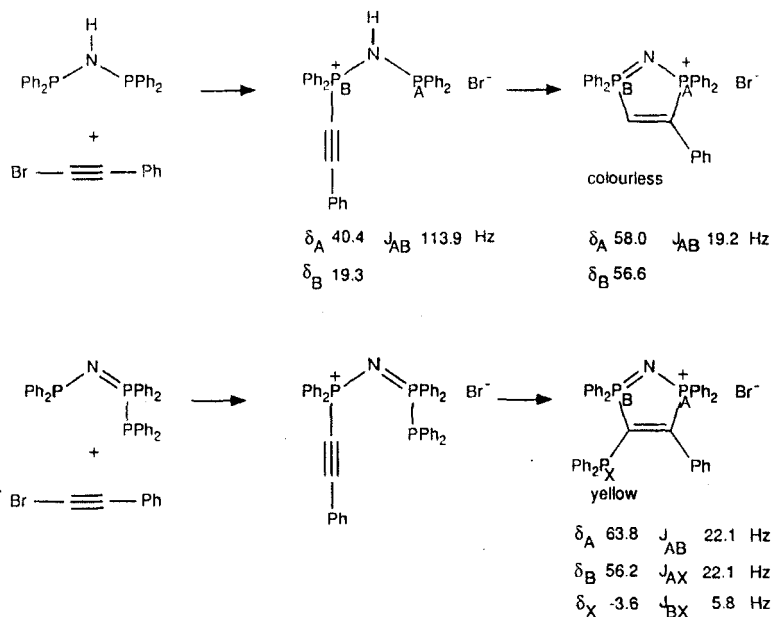
ALFRED SCHMIDPETER, MARTIN THIELE, JOHANNA STOCKER
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Our attempt to synthesize 1,2λ⁵,5λ⁵-azadiphospholium ions by a cycloaddition reaction analogous to that leading to 1,2λ⁵-azaphospholines¹ was not successful.

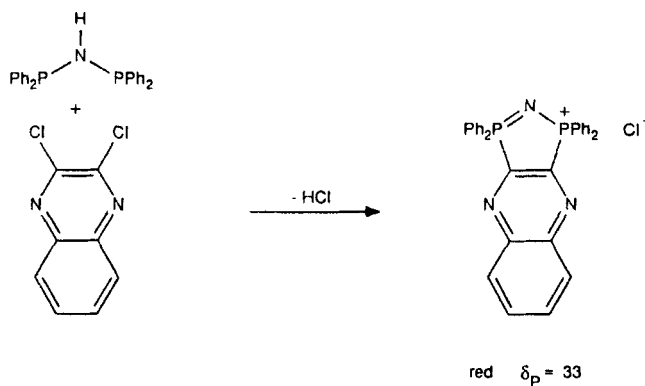


An effective route is provided by the reaction of the bis(diphenylphosphino)amine and a haloacetylene as demonstrated for the phenylbromoacetylene. As an intermediate the alkynylphosphonium bromide is observed in the ³¹P NMR spectrum. An intramolecular nucleophilic attack of the second phosphino group onto the carbon β to the phosphonium center and a 1, 3-proton shift completes the reaction.

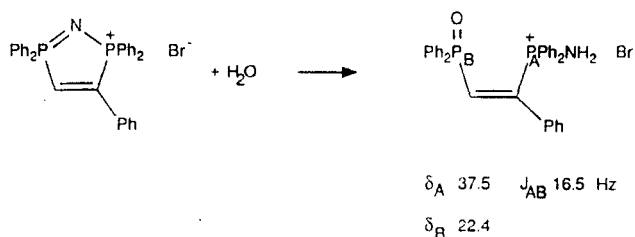


From the tetraphenyldiphosphine diphenylphosphinoimine a bright yellow diphenylphosphino derivative is obtained.

A further synthetic possibility gives the reaction of the diposphinoamine with an unsaturated 1, 2-dihalide. It was successful in case of 2, 3-dichloroquinoxaline yielding a tricyclic azadiphospholium chloride in red crystals.

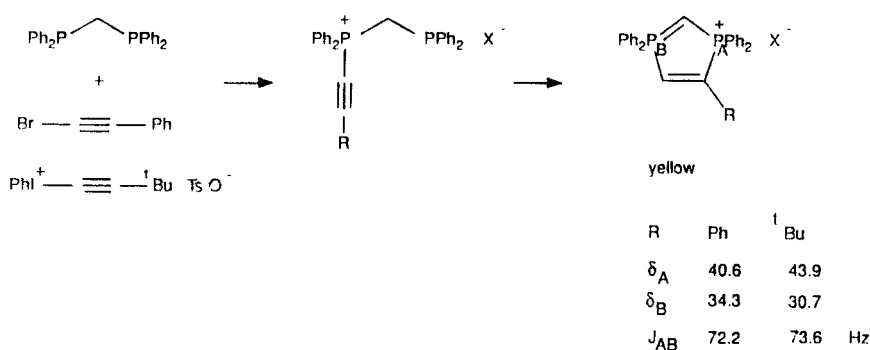


The azadiphospholium ions are not particularly moisture sensitive, but hydrolyze with water in solution. This is in contrast to the widely used acyclic hexaphenyl-diphosphazanium ion which is stable to hydrolysis. In the hydrolysis the azadiphospholium ring is opened at a PN-bond resulting in a phosphinoylvinyl-aminodiphosphonium ion.



The 4-phenylazadiphospholium ring is opened selectively at the 1,2-bond. This is explained by the mechanism which is discussed in detail for the hydrolysis of the diphospholium ions (see below).

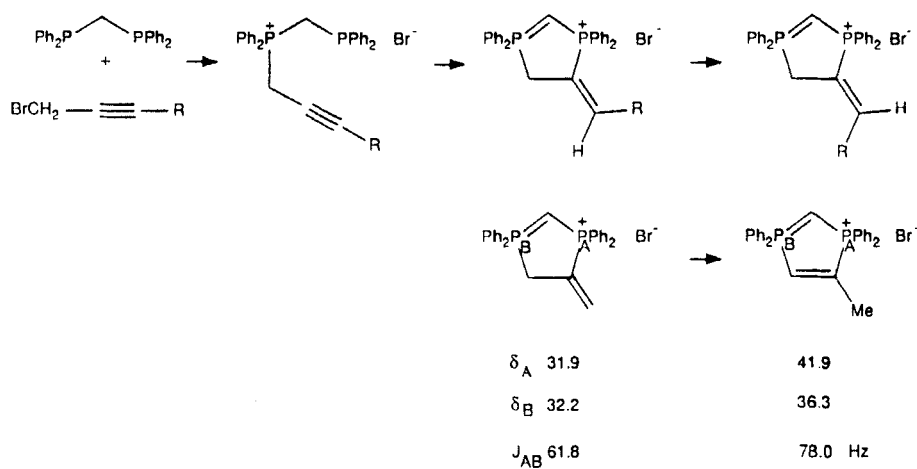
Bis(diphenylphosphino)methane like the diphosphinoamine adds phenylbromoacetylene yielding the 4-phenyl-diphospholium bromide. The 4-tert.butyl derivative is formed with the respective ethynylidonium tosylate².



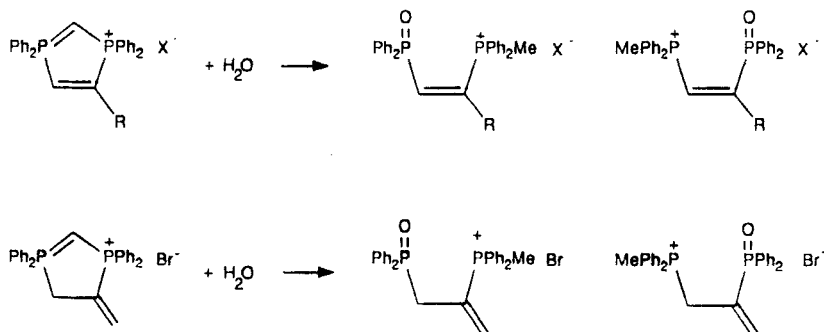
As a first stage again an alkynylphosponium ion is expected but cannot be detected spectroscopically.

The 4-methyldiphospholium ion is obtained from the reaction of the diphosphinomethane with propargyl bromide³. Propargyl bromides initially give the respective phosphonium bromides which isomerize to the diphosphafulvenium salts. For R = Ph the *Z*-form is kinetically favoured but converts eventually to the *E*-form.

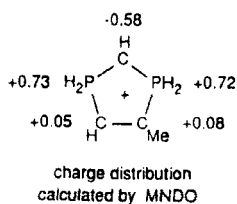
In case of R = H base catalysis converts the diphosphafulvenium ion further to the methyldiphospholium ion.



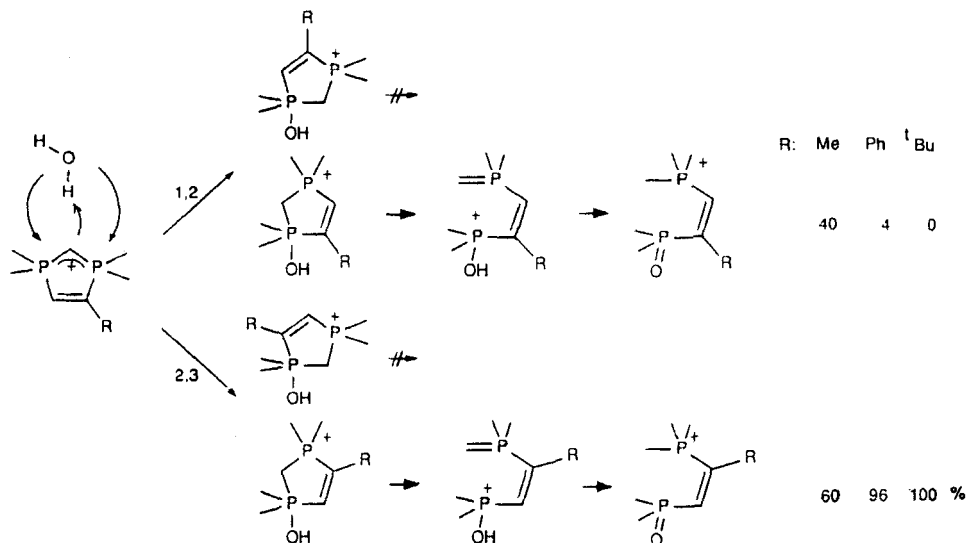
Both diphospholium and diphosphafulvenium ions hydrolyze readily; in every case the PCP unit is opened preferentially at the 1,2-bond.



R_2P groups are isoelectronic but not isolobal to RC groups. Where the two are combined negative charge is transferred from phosphorus to carbon. This is found to be true again for the diphospholium ring from the calculated charge distribution which should be compared to that of the carbocyclic cation, i.e. the cyclopentadienyl cation.



As already suggested by the bond representation negative charge accumulates at C-2. Consequently diphospholium ions are protonated at C-2. Hydrolysis also most probably starts with a proton transfer to this position, followed by a hydroxide addition to one of the phosphorus atoms. As is well known⁴, the five-membered ring facilitates the phosphorus to become five-coordinate. In the resulting TBP coordination it always occupies the axial-equatorial position.



For the suggested addition of water to a PC-bond a 4-substituted diphospholium ion offers four different possibilities. In the next step the axial PC-bond of the ring will open, putting a negative charge on carbon. This will occur most readily where this charge is stabilized by an adjacent phosphonium center. As a consequence the ring is opened selectively at the PCP unit. Which of the two bonds of this unit is preferentially opened obviously depends on the 4-substituent which hinders more or less the hydroxide addition to phosphorus.

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