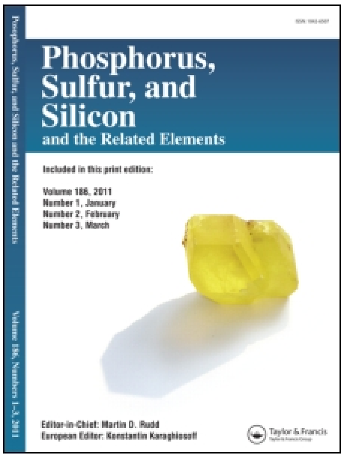

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Photolysis of Phosphoniums and Phosphoranes Azides

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PHOTOLYSIS OF PHOSPHONIUMS AND PHOSPHORANES AZIDES

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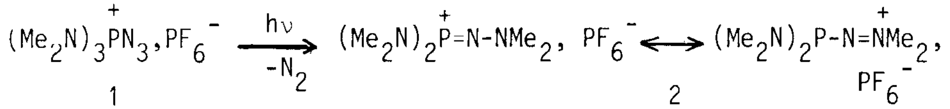
Abstract First evidence for a Curtius type rearrangement involving a pentacoordinated atom and charged species are described

In organic chemistry the Curtius rearrangement is a well known method for obtaining imines and isocyanates from the corresponding azides ([1, 2]). Various transient unusually hybridized organometallic species were also obtained using this rearrangement which proved to be a general method allowing the coordination number of the atom bonded to the azido group to be decreased by one unit, keeping the number of valence bonds unchanged.

Up to now no examples of a Curtius type rearrangement involving a charged atom or a pentacoordinated atom have been described. Here we wish to report i) the synthesis of unusually hybridized phosphorus cations from azidophosphonium salts ii) the results observed during the photolysis of some pentacoordinated pentavalent phosphorus azides.

AZIDO PHOSPHONIUM SALTS

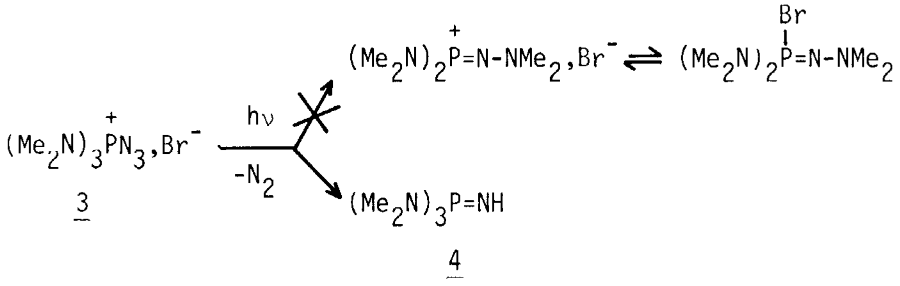
Irradiation of tris(dimethylamino) azidophosphonium hexafluoro phosphate 1 leads to the imino phosphenium salt 2 with release of nitrogen [2 $\delta^{31}P = +77$; ^{1}H 2.73 (d, $J_{PH} = 11$ Hz, 12H, CH_3-N-P), 3.20 (s, 6H, N-NCH_3)].



$$(Me_2N)_3\overset{+}{P}N_3, PF_6^- \xrightarrow[-N_2]{h\nu} (Me_2N)_2\overset{+}{P}{=}N{-}NMe_2,\ PF_6^- \longleftrightarrow (Me_2N)_2P{-}N{=}\overset{+}{N}Me_2,\ PF_6^-$$

1 2

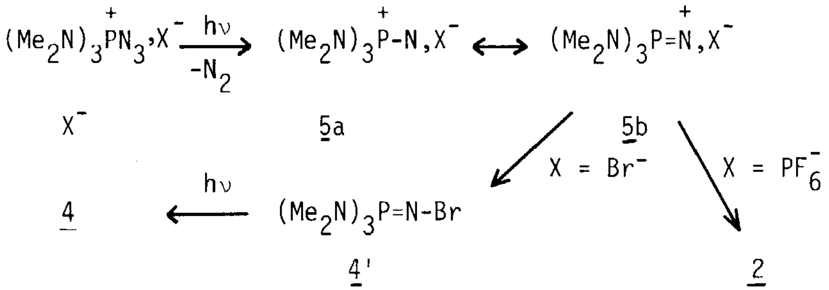
In order to study the importance of the anion in this reaction, compound 3 was irradiated in the same experimental conditions. We observed the formation of iminophosphorane 4 with a 80% yield.


$(Me_2N)_3\overset{+}{P}N_3,Br^- \xrightarrow[-N_2]{h\nu}$ $(Me_2N)_2\overset{+}{P}=N-NMe_2,Br^- \rightleftharpoons (Me_2N)_2\overset{Br}{P}=N-NMe_2$; $(Me_2N)_3P=NH$

3

4

This dramatic change in the course of the photolytic reaction, due to the nature of the anion, can be well rationalized by the transient existence of a phosphonium nitrene 5a in resonance form with a phosphonitrenium 5b


$(Me_2N)_3\overset{+}{P}N_3,X^- \xrightarrow[-N_2]{h\nu} (Me_2N)_3\overset{+}{P}-N,X^- \longleftrightarrow (Me_2N)_3P=\overset{+}{N},X^-$

X^- 5a 5b

X = Br^- ; X = PF_6^-

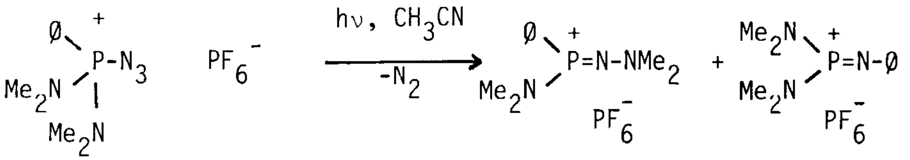
4 $\xleftarrow{h\nu}$ $(Me_2N)_3P=N-Br$

4'

2

When the anion is a poor nucleophile such as PF_6^- , the intermediate 5 is stabilized by migration of one phosphorus substituent onto the nitrogen atom with formation of iminophosphenium salt 2. On the other hand,the good nucleophilicity of the bromine anion leads to the formation of derivative 4' which gives by subsequent irradiation the iminophosphorane 4.

Irradiation of the azidophosphonium 7 leads to the formation of 8 and 9 (migration of a dimethylamino group or a phenyl group)

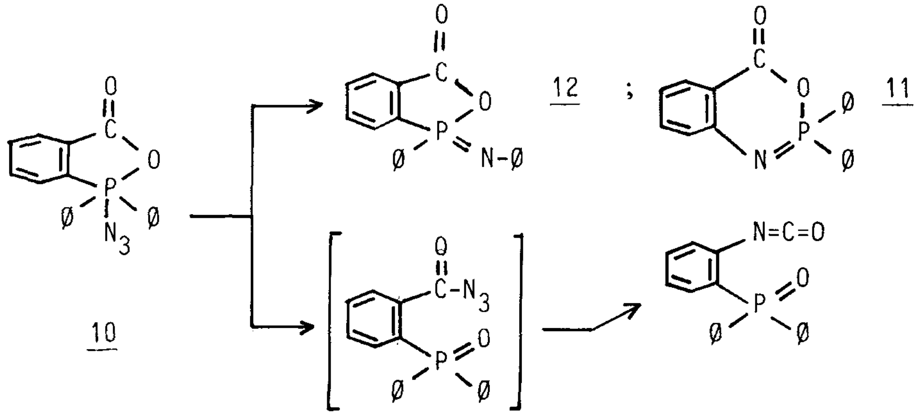


7 $\delta^{31}P$ = +46 ppm 8 $\delta^{31}P$ = +70 ppm 9 $\delta^{31}P$ = +41ppm

8 is the first example of an iminophosphenium salt with a P-C bond.

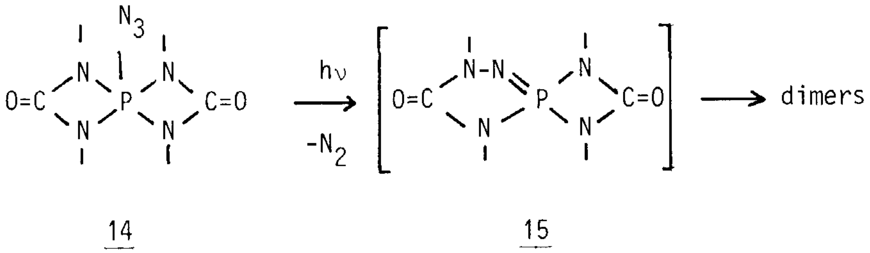
PENTACOORDINATED PENTAVALENT PHOSPHORUS AZIDES

10 slowly decomposes at room temperature leading, neither to the expected ring expansion product 11, nor to derivative 12 which would have resulted from the migration of a phenyl group from the phosphorus atom to the nitrogen atom, but to the isocyanate 13 in 80% yield.

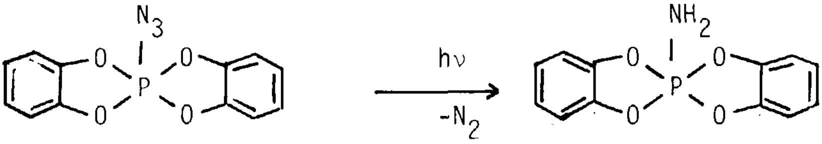


$\delta^{31}P$ = -60 ppm 13 $\delta^{31}P$ = +28ppm

On the other hand irradiation of the stable novel azido phosphorane 14 (the first one in which phosphorus is bonded to five nitrogen atoms) in acetonitrile solution, at 254 nm, at room temperature leads quantitatively to the formation of the very short lifetime intermediate 15.



One can conclude that the Curtius rearrangement is also effective with a pentacoordinated phosphorus atom. However this rearrangement is strongly dependent of the nature of the phosphorus substituent. Thus irradiation of the azide 16 gives 17 as the major compound. This result is not surprising taking into account the poor migrating aptitude of alcoxy group, the main reaction being here the abstraction of protons from the solvent by a transient nitrene



16 $\delta^{31}P = -27ppm$ 17 $\delta^{31}P = -27ppm$

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(2) Baceiredo A., Majoral J.P., Bertrand G., Nouv. J. Chim. (1983), 4, 255.

(3) The synthesis of the first stable iminophosphenium salt was recently reported by Marre et al : Sanchez M. , Marre M.R., Brazier J.F., Bellan J., Wolf R. , Phosphorus Sulfur (1983) 14 331 and ref. included.