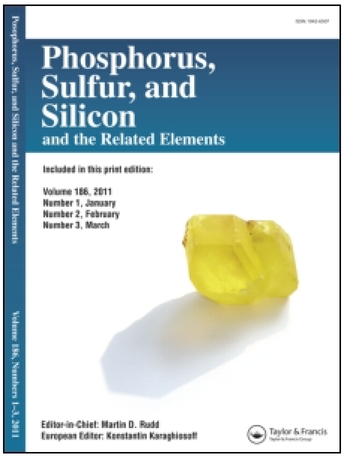

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PHOSPHORUS-NITROGEN TRIPLE-BONDED SPECIES

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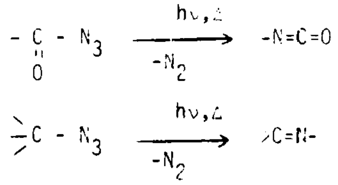
Evidence for the transient formation of new phosphorus-nitrogen triple bonded species are given. Rules concerning the photolytic and thermolytic behavior of azides are reported.

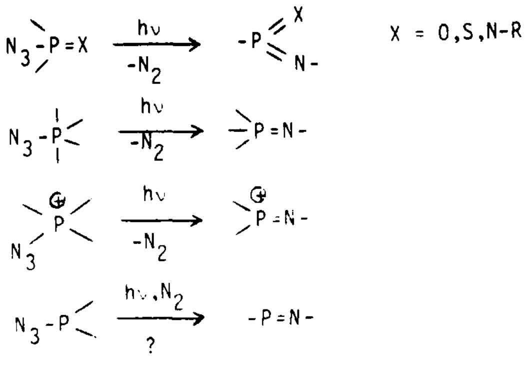
It is well known that the photolytic, thermolytic or acid promoted rearrangement of organic azides afford imines and isocyanates. This reaction named as the Curtius rearrangement allows the coordination number of the carbon atom bonded to the azido group to be decreased by one unit keeping the number of valence bonds unchanged



Based on these results it was tempting to try to prepare various azides in which the carbon atom is replaced by silicon, germanium, phosphorus, arsenic etc... and to see if the Curtius rearrangement is effective within these systems as well. If it is, we should obtain new or rare organometallic species.

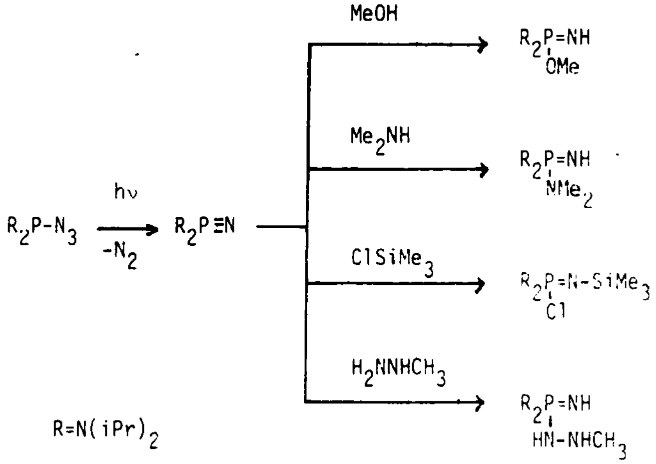
Although we examined a lot of reactions involving silicon, germanium and arsenic azides, only our results concerning the thermal and photochemical behavior of phosphorus azides will be presented.

We have previously shown[1] that the Curtius rearrangement is effective for tetracoordinated pentavalent phosphorus derivatives, pentacoordinated pentavalent phosphorus compounds and for cationic species such as phosphonium salts.

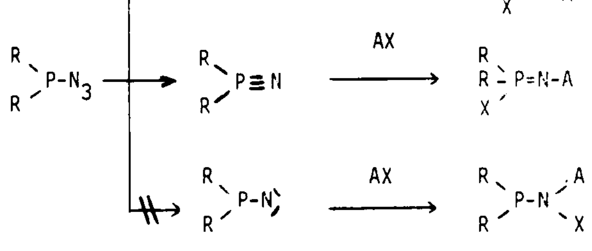


The subject was inviting to extend the reaction—in order to determine the scope and limitation of these experiments—to the photochemical behaviour of azides in which the azido group is bonded to a tricoordinated trivalent phosphorus atom. We should observe in this case the formation of dicoordinated phosphorus species with various substituents on phosphorus. Nevertheless an ab initio study of all the H_2PN isomers in their low lying singlet and triplet states[2] indicated that the structure of a singlet phosphinonitrene supports a phosphonitrile notation $H_2P{\equiv}N$, due to delocalization of the lone pairs $n_{\Pi}(P) \rightarrow p_{\Pi}(N)$ and $n_{\Pi}(N) \rightarrow d_{\Pi}(P)$. In order to see if it was possible to generate such a phosphonitrile we prepared the bis(diisopropylamino)phosphine azide previously described by Scherer *et al.*[3] This azide is perfectly stable and can be distilled. The presence of bulky substituents masking the phosphorus lone pair is certainly responsible of the absence of a Staudinger reaction.

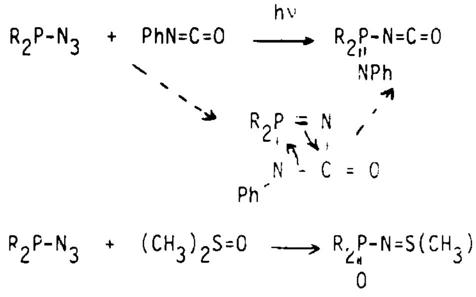
The photolytic reactions were carried out in benzene solution at 300 nm at room temperature in the presence of a stoichiometric amount of trapping agent such as methanol, dimethylamine, trimethylchlorosilane[4] or methylhydrazine. The products, obtained in near quantitative yield, can be considered as the result of the 1-2 addition of the trapping agent on a transient phosphorus-nitrogen triple-bonded species.



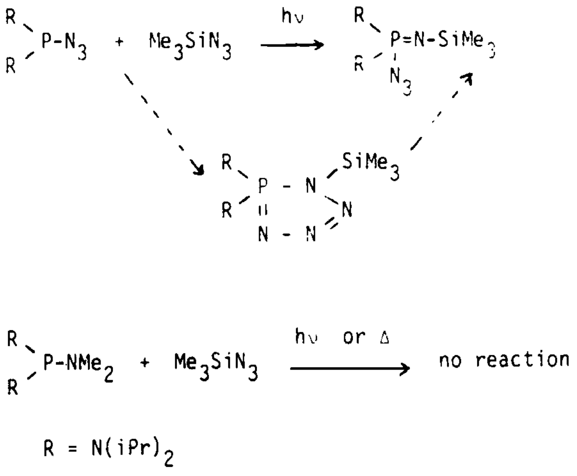
We never observed a Curtius type rearrangement that is to say a migration of a diisopropylamino group from phosphorus to nitrogen followed by 1-2 addition of the trapping agent onto the phosphorus-nitrogen double bond. Furthermore we never observed the formation of a compound resulting from 1-1 addition of the trapping agent AX on a transient phosphinonitrene.



A [2 + 2] cycloaddition reaction is observed during the photolysis of the bis(diisopropylamino)phosphine azide in presence of phenyl isocyanate. The four-membered ring, thus obtained, is photochemically unstable and rearranges into a phosphorus isocyanate. A similar cycloaddition occurred with dimethyl sulfoxide.



Irradiation of the starting azide in presence of azidotrimethylsilane led to the formation of a linear phosphazene.

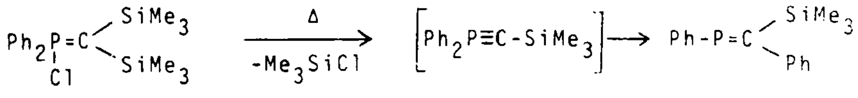


In a first approach we might think that only a Staudinger reaction takes place. In fact this reaction is only photochemically induced and fails when the two azides are heated together. Taking into account that i) the Staudinger reaction is a thermal reaction ii) there is no thermal or photochemical reaction when the azido group of the phosphine is replaced by a dimethylamino group, we can conclude that the linear phosphazene is formed via a [2 + 3] cycloaddition reaction, which gives rise to a transient five-membered ring which rearranges.

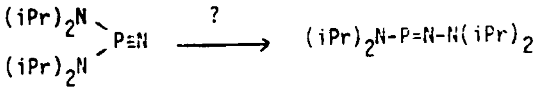
These results, on the whole, showed that a λ^3 phosphinonitrene reacts as a nitrilo λ^5 phosphane.

A question remained: what would be the fate of the phosphonitrile in the absence of any trapping agent?

Appel *et al.*[5] postulated the transient existence of a λ^5-phosphaacetylene to rationalize the formation of a phosphaalkene in the following reaction:



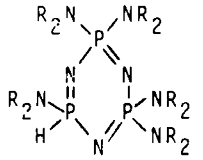
Thus one could imagine that the phosphonitrile would rearrange to give a dicoordinated phospha-imine.

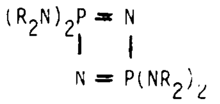


$$(iPr)_2N-P=N-N(iPr)_2$$

Note that this hypothesis could be consistent with the results observed in the cophotolysis of the bis(diisopropylamino)phosphine azide with trapping agents since the lifetime of the phosphonitrile is sufficient to allow trapping reactions.

When the azide was irradiated in toluene solution at 300 nm at low temperature, for 8 hours, three products were detected by ^{31}P NMR spectroscopy. One of the signals (δ $^{31}P = +246$ ppm) slowly disappears after a few hours. The two other products were isolated and characterized as a pentaaminohydridocyclotriphosphazene (3% yield) and a tetraaminocyclodiphosphazene (42% yield).[6]





The structure of the dimer has been clearly established by a single X-ray diffraction study. The four-membered ring is organized around a symmetry center implying the absolute planarity of the ring. All endo and exocyclic phosphorus-nitrogen bond lengths are equal (from 1.644 to 1.651 Å) indicating that the unsaturation is strongly delocalized.[6]

Although several hundred cyclo tri-, tetra- and polyphosphazenes are known, up to now, no examples of cyclodiphosphazenes have been reported. The non-existence of these cyclic dimeric species has mainly been explained in terms of ring strain and contraction of the N—P—N bond angles below 115–120° which could cause serious interpenetration of the nitrogen Van der Waals boundaries.

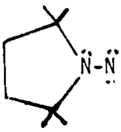
The surprising stability of the first isolated "heterocyclobutadiene" is probably due to the high thermodynamic energy of the corresponding monomer preventing dissociation and to steric factors which hinder polymerization.

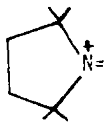
Another question remained: what was the structure of the compound with a ^{31}P chemical shift of +246 ppm? In a first approach, this chemical shift is in good agreement with that expected for the dicoordinated phosphorus derivative which would be obtained via a Curtius type rearrangement. On the other hand, it is very difficult to predict the ^{31}P chemical shift of a phosphonitrile since, as far as we know, no tricoordinated phosphorus triple bonded derivatives have yet been spectroscopically characterized.

To tentatively assign this signal, methanol, dimethylamine or chlorotrimethylsilane were added at −40°C to the photochemical reaction mixture obtained after two hours of irradiation at −40°C. Beside the signals corresponding to the starting azide and cyclodiphosphazene, the singlets corresponding to the expected adducts of the phosphonitrile were observed.

Thus it seems quite likely that the phosphonitrile presents a ^{31}P chemical shift of +246 ppm, has a half lifetime of about 12 hours at room temperature and is stable for several days at −40°C. Its dimerization is probably induced by U.V. irradiation.

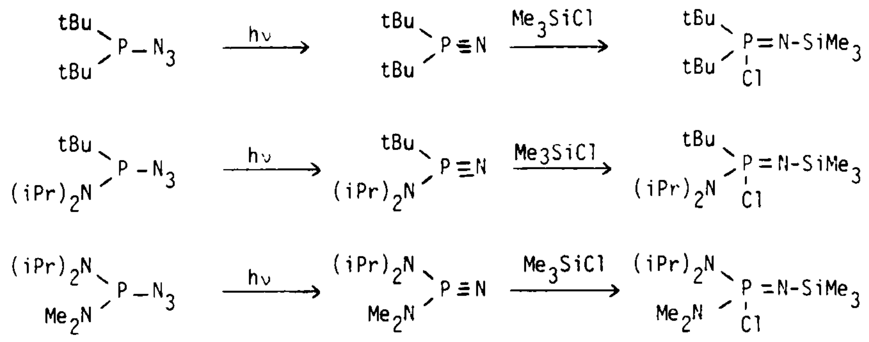
The relative stability of this first phosphorus-nitrogen triple-bonded species is not really astonishing since Dervan *et al.*[7] reported that, in contrast with alkyl or arylnitrenes, some amino-nitrenes (diazenes) are stable for days at −78°C: the multiple character of the nitrogen-nitrogen bond explains the stabilization of the nitrene species.



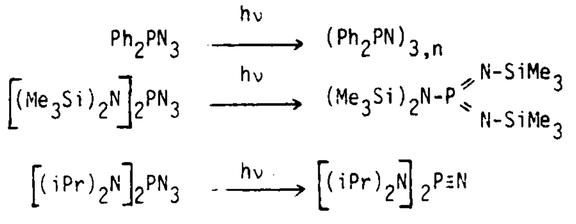


So we think that we provide the first spectroscopic evidence for a new class of nitrene: phosphinonitrene stabilized as phosphonitrile.

Three other transient phosphonitriles were trapped with trimethylchlorosilane during the photolysis of three new phosphine azides bearing at least one bulky substituent.



So it is clear that no Curtius rearrangement takes place during the photolysis of phosphine azides. Depending on the nature of the substituents three types of reaction can be observed.

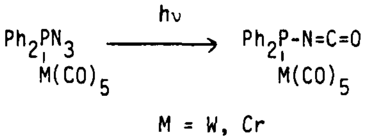


—The first one involves a Staudinger reaction with the formation of cyclo tri-, tetra- or pentaphosphazenes.

—The second is a trimethylsilyl group migration from a nitrogen to another nitrogen with the formation of tricoordinated pentavalent phosphorus compounds.[8]

—The third one leads to a phosphonitrile.

Since all these reactions involve the phosphorus lone pair electrons, one might anticipate that the complexation of the phosphorus atom encourages the Curtius type rearrangement and thereby provides a facile route to iminophosphane complexes. In fact irradiation of a toluene or acetonitrile solution of diphenyl azidophosphine complexes gave rise to phosphine isocyanate complexes. It seems reasonable that this reaction proceeds via the transient formation of a phosphinonitrene intermediate which combines with carbon monoxide.



$$\underset{M(CO)_5}{Ph_2PN_3} \xrightarrow{h\nu} \underset{M(CO)_5}{Ph_2P\text{-}N{=}C{=}O}$$

$M = W, Cr$

In conclusion we have shown that the Curtius rearrangement takes place during the photolysis of P_{IV}, P_V compounds and phosphonium salts but failed in the case of P_{III} derivatives.

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