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Photochemical and Thermal Rearrangement of Heavier Main-Group Element Azides

GUY BERTRAND,* JEAN-PIERRE MAJORAL,* and ANTOINE BACEIREDO

U.A. 477 and U.A. 454, Université Paul Sabatier, 31062 Toulouse Cédex, France

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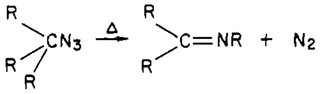
Organic azides have been known since 1864.[1] As early as 1890 Curtius[2] reported that heating of acyl azides in inert solvents leads to the corresponding isocyanates with loss of nitrogen (eq 1).

$$RC(O)N_3 \xrightarrow{\Delta} RN{=}C{=}O + N_2 \qquad (1)$$

This observation stimulated a significant volume of research over the next decades,[3] and it appeared that this type of rearrangement had a broad scope of applications. Indeed thermolytic, photolytic, or acid-promoted rearrangement of linear or cyclic aliphatic, aromatic, or heteroaromatic azides affords the corresponding carbon–nitrogen double-bonded compounds (eq 2).



(2)

In contrast, although some heavier main-group element azides have also been known for a long time,[4] it is only in the last few years that their thermal and photochemical behaviors have been intensively investigated.

Like organic azides, organometallic azides are covalently bonded. However, their physical and chemical properties vary over a wide range and in some cases bear considerable resemblance to those of ionic azides. It is of particular interest that only azides of boron, silicon, germanium, phosphorus, and arsenic are known to lose two-thirds of their azide nitrogen by pyrolysis, leading to a metal–nitrogen bond (eq 3), while the other organometallic azides including aluminum, tin, lead, and antimony lose three atoms of nitrogen, leaving no metal–nitrogen bonds (eq 4).

$$\underset{\mathbf{A}}{R_nMN_3} \xrightarrow{\Delta} (R_nMN) + N_2 \qquad (3)$$
$$M = B, Si, Ge, P, As$$

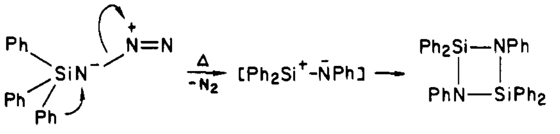
$$\underset{\mathbf{B}}{R_nM'N_3} \xrightarrow{\Delta} (R_nM') + {}^3/_2N_2 \qquad (4)$$
$$M' = Al, Sn, Pb, Sb$$

In the last few years, a considerable number of papers have been devoted to the synthesis of unusually hybridized heavier main-group element derivatives[5] (—B=, >Si=, —P=, —P(=)$_2$...). Since in organic chemistry, the Curtius rearrangement allows an sp^3-hybridized carbon to be transformed into the corresponding sp^2 (eq 2) or alternatively an sp^2 into an sp (eq 1), these rearrangements were extrapolated to heavier main-group elements (obviously only azides of type **A** have the possibility of undergoing this transformation).

Caution! Azides present extreme risk of explosion by shock, friction, or heating; maximum care must be taken.

Group 14 Azides

A Curtius-type rearrangement in the silicon series was first claimed by Reichle in 1964.[6] With reference to the formation of 1,1,2,3,3,4-hexaphenylcyclodisilazane in the thermolysis of triphenylsilyl azide, he postulated the transient existence of a zwitterionic species resulting from the migration of a phenyl group from silicon to carbon with loss of nitrogen (eq 5).



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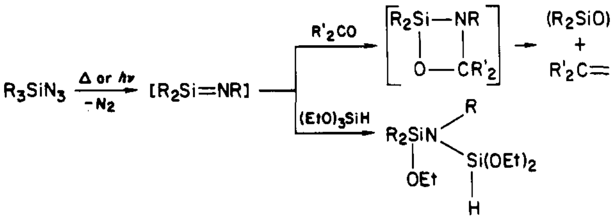
Sommer et al.[7] characterized transient sila imines by a trapping reaction in the photolysis or thermolysis of various silicon azides (eq 6).



(6)

Guy Bertrand was born in Limoges, France, in 1952. He graduated (ingénieur ENSCM) from the University of Montpellier and presented his Thèse d'Etat at the University of Toulouse in 1979. He is now Chargé de Recherche CNRS at the University Paul Sabatier of Toulouse. His current research interests include unusually hybridized main-group element species, phosphinidene complexes and phospholipid chemistry.

Jean-Pierre Majoral, a native of Montauban, France, is Directeur de Recherche CNRS. He presented his Thèse de 3e cycle in 1967 and his Thèse d'Etat in 1972 at the University Paul Sabatier of Toulouse. His current research interests include low-coordinated heavier main-group elements and heterocyclic chemistry.

Antoine Baceiredo was born in 1954 at Cambre, Spain. He moved to France in 1960. He presented his Thèse de 3e cycle in 1982 and his Thèse d'Etat in 1984 at the University Paul Sabatier of Toulouse. He is currently doing post-doctoral work at the University of Southern California in Los Angeles.

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[3] Patai, S. "The Chemistry of the Azido Group"; Wiley-Interscience: New York, 1971. Lwowski, W. "Nitrenes"; Wiley-Interscience: New York, 1970. Scriven, E. F. V. "Azides and Nitrenes: Reactivity and Utility"; Academic Press: New York, 1984.

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[5] Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529. Bertrand, G.; Trinquier, G.; Mazerolles, P. *Organomet. Chem. Rev.* **1981**, *12*, 1. Coleman, B.; Jones, M. Jr. *Rev. Chem. Intmed.* **1981**, *4*, 297. Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731. Cowley, A. H. *Acc. Chem. Res.* **1984**, *17*, 386. Gaspar, P. P. "Reactive Intermediates"; Jones, M., Moss, R. S., Eds.; Wiley: New York, 1978. Fluck, E. *Top. Phosphorus Chem.* **1980**, *10*, 193. Regitz, M.; Mass, G. *Top. Curr. Chem.* **1981**, *97*, 71. Satgé, J. *Adv. Organomet. Chem.* **1982**, *21*, 241.

[6] Reichle, W. T. *Inorg. Chem.* **1964**, *3*, 402.

[7] Parker, D. R.; Sommer, L. H. *J. Am. Chem. Soc.* **1976**, *98*, 618. Parker, D. R.; Sommer, L. H. *J. Organomet. Chem.* **1976**, *110*, C1. Elsheikh, M.; Pearson, N. R.; Sommer, L. H. *J. Am. Chem. Soc.* **1979**, *101*, 2491.

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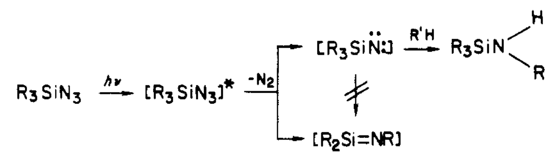
Unambiguous proof for the Curtius rearrangement in the silicon series has been reported very recently by West et al.,[8] who have found that irradiation of trimesitylazidosilane at low temperatures yields the yellow sterically hindered trimesityl sila imine, which is stable at a low-temperature solution up to about −130 °C (eq 7).

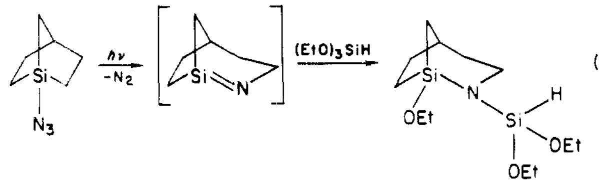
$$(\mathrm{Mes})_3\mathrm{SiN}_3 \xrightarrow{h\nu} \mathrm{Mes}_2\mathrm{Si{=}NMes} \qquad \lambda_{\max} = 439\ \mathrm{nm} \tag{7}$$

From a mechanistic point of view, although we have provided evidence for the transient existence of silylnitrenes by insertion reactions in carbon–hydrogen bonds,[9] it seems quite likely that the formation of sila imines involves a non-nitrene mechanism (eq 8). Just as in the carbon series,[10] only a concerted migration–nitrogen loss mechanism can satisfactorily explain the difference in the migrating aptitude of silicon substituents.



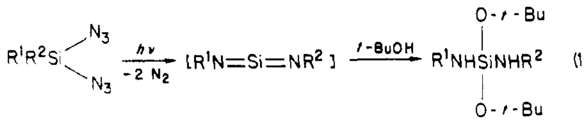
(8)

Some synthetic applications of the Curtius-type rearrangement in this series have already been reported. Sommer[11] and ourselves[9] have synthesized, via ring-expansion reactions, original difunctionalized heterocycles that are extremely difficult to obtain by classical routes (eq 9).



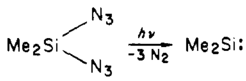
(9)

Ando[12] postulated the transient formation of silacarbodiimides, resulting from a double-Curtius rearrangement, in the photolysis of geminal diazides (eq 10).


(10)

$$\mathrm{R^1R^2Si(N_3)_2} \xrightarrow[-2\,\mathrm{N_2}]{h\nu} [\mathrm{R^1N{=}Si{=}NR^2}] \xrightarrow{t\text{-BuOH}} \mathrm{R^1NHSi(O\text{-}t\text{-}Bu)_2NHR^2}$$

However, the possibility that this happens strikes us as remote, considering the undoubtedly short lifetime of the initially formed sila imine in the presence of *tert*-butyl alcohol. Thus, we prefer a two-step mechanism. Moreover, it is noteworthy that the irradiation of diazidodimethylsilane in matrix-isolation produces considerable yields of dimethylsilylene (eq 11).[13]


(11)

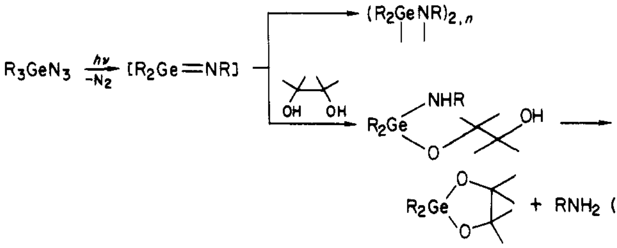
$$\mathrm{Me_2Si(N_3)_2} \xrightarrow[-3\,\mathrm{N_2}]{h\nu} \mathrm{Me_2Si:}$$

Silicon azides also appeared to be suitable precursors for the first triply bonded silicon-containing species. Indeed, as early as 1966 it was reported that photolysis of silyl or trideuteriosilyl azides, in solid argon matrices near 4 K, leads to the corresponding sila isonitrile (eq 12).[14] Recently, an analogous species was observed in a photoelectron spectrometer during the examination of the pyrolysis products of phenyltriazidosilane (eq 13)[15] as well as by UV and IR spectroscopies in the photolysis of the same compound in an argon matrix.[16]

$$\mathrm{H_3SiN_3} \xrightarrow[-\mathrm{N_2}]{h\nu} \mathrm{Si{\equiv}NH} \tag{12}$$

$$\mathrm{PhSi(N_3)_3} \xrightarrow[-4\,\mathrm{N_2}]{\Delta\ \text{or}\ h\nu} \mathrm{Si{\equiv}NPh} \tag{13}$$

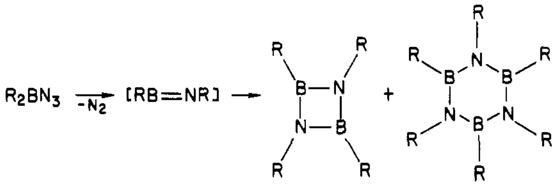
In contrast with silicon azides, few papers have been devoted to the decomposition of germanium azides.[8] We proved that the Curtius rearrangement is also effective in the germanium series.[17] Indeed, photolysis of trialkyl- or triarylazidogermanes affords transient germa imines that dimerize or polymerize in the absence of trapping agents and react with, for example, pinacol, to give germadioxolanes along with the corresponding amine (eq 14).



(14)

Boron Azides

Thermolysis of azidoboranes, in gas phase or in solution, appears to be a quite general method for obtaining iminoboranes. Numerous examples of Curtius-type rearrangements involving alkyl-, aryl-, or amino-substituted boron azides have been reported by Paetzold and co-workers.[18] Iminoboranes are usually unstable and dimerize or trimerize, giving the corresponding diazadiboretidines (1) or borazines (2) (eq 15).



1 2 (15)

However, examples of iminoboranes that are stable at

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(8) West, R.; Zigler, S.; Michl, J.; Gross, G. Presented at the XIXth Organosilicon Symposium, Louisiana State University, Baton Rouge, LA, Apr 26–27, 1985.

(9) Baceiredo, A.; Bertrand, G.; Majoral, J. P.; Mazerolles, P. *Nouv. J. Chim.* 1983, *7*, 645.

(10) Kyba, E. P.; Abramovitch, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 735.

(11) Elsheikh, M.; Sommer, L. H. *J. Organomet. Chem.* **1980**, *186*, 301.

(12) Ando, W.; Tsumaki, H.; Ikeno, M. *J. Chem. Soc., Chem. Commun.* 1981, 597.

(13) Vancik, H.; Raabe, G.; Michalczyk, M. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1985**, *107*, 4097.

(14) Ogilvie, J. F.; Craddock, S. *J. Chem. Soc., Chem. Commun.* **1966**, 364.

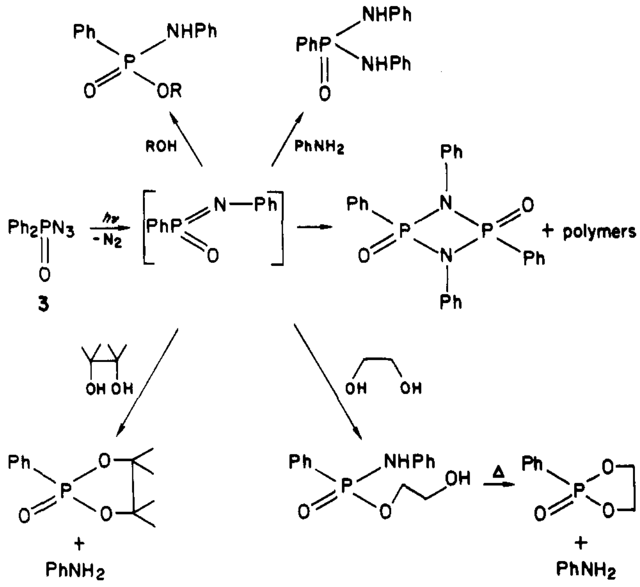
(15) Bock, H.; Dammel, R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 111.

(16) Gross, G.; Michl, J.; West, R. Presented at the XIXth Organosilicon Symposium, Louisiana State University, Baton Rouge, LA, Apr 26–27, 1985.

(17) Baceiredo, A.; Bertrand, G.; Mazerolles, P. *Tetrahedron Lett.* **1981**, *22*, 2553.

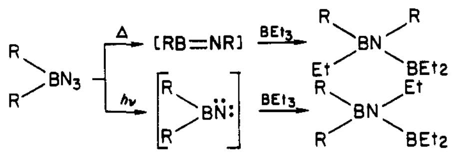
(18) (a) Paetzold, P. I. Fortschr. *Chem. Forsch.* **1967**, *8*, 437. (b) Pieper, W.; Schmitz, D.; Paetzold, P. *Chem. Ber.* **1981**, *114*, 3801. (c) Paetzold, P.; Truppat, R. *Chem. Ber.* **1983**, *116*, 1531. (d) Meier, H. U.; Paetzold, P.; Schröder, E. *Chem. Ber.* **1984**, *117*, 1954.

Scheme I



room temperature have been recently reported.[19] Their structural properties are comparable to those of isoelectronic alkynes: linearity of the molecule, very short boron–nitrogen bond (1.26 Å), and a ^{11}B–N IR vibration at 2010–2020 cm^{-1}. So, iminoboranes are better formulated as RB≡NR.

Formation of borylnitrene is a minor pathway in the thermolysis of azidoboranes. In contrast, under photolytic conditions, bis(diisopropylamino)azidoborane almost exclusively generates the nitrene as shown by trapping with triethylborane (eq 16).[18b]



(16)

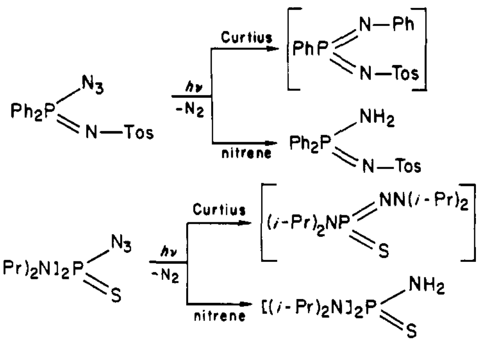
Phosphorus Azides

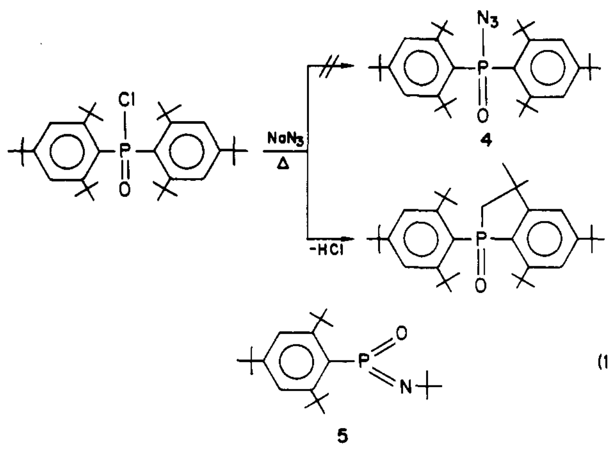
We have seen in the first part of this paper that the rearrangement of tri- and tetracoordinated azido derivatives often leads to a change in the coordination number of the atom bearing the N_3 group. Because of the variety of its known and potentially available hybridization states, the phosphorus atom was an interesting model to study the scope and limitations of such rearrangements.

Tetracoordinated Pentavalent Phosphorus Azides. The readily available oxide of diphenylphosphine azide (3) was chosen as a model to study the photochemical behavior of azidophosphine oxides. The products obtained by irradiation of 3 in the presence or absence of trapping agents clearly demonstrated that the migration of a phenyl substituent from the phosphorus to the nitrogen atom occurred with loss of N_2 (Scheme I).[20]

This is a quite general method for the synthesis of transient oxoiminophosphorane.[21] The only difficulty is in the synthesis of the starting azide. For instance, we could not prepare the azide of bis(2,4,6-tri-*tert*-butylphenyl)phosphine oxide (4) (eq 17),[22] and so this method is probably not suitable for the synthesis of stable oxoiminophosphorane, which requires extremely bulky substituents. Until now, only **5**, prepared in another way, was found stable enough to be spectroscopically characterized.[23]

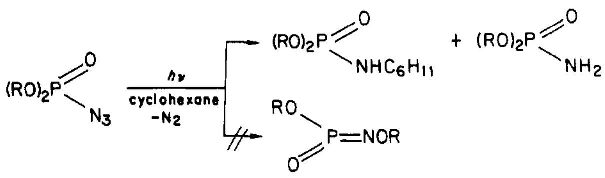
Scheme II





(17)

As for the groups 13 and 14 azides considered above competitive nitrene-type reactions are sometimes observed,[21] but usually as the minor pathway. However, in the case of dialkoxy-substituted phosphine oxides, no migration occurred and only nitrene-type products were observed (eq 18).[21i,j]



(18)

There are many similarities in the photochemical behavior of azidophosphine oxides and their thio and imino analogues (Scheme II).[21a,b]

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[19] (a) Paetzold, P.; Von Plotho, C.; Schmid, G.; Boese, R.; Schrader, B.; Bougeard, D.; Pfeiffer, U.; Gleiter, R.; Schäfer, W. *Chem. Ber.* **1984**, *117*, 1089. (b) Haase, M.; Klingebiel, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 324. (c) Paetzold, P.; Von Plotho, C. *Chem. Ber.* **1982**, *115*, 2819.

[20] Bertrand, G.; Majoral, J. P.; Baceiredo, A. *Tetrahedron Lett.* **1980**, *21*, 5015. Majoral, J. P.; Bertrand, G.; Baceiredo, A.; Mazerolles, P. *ACS Symp. Ser.* **1981**, *171*, 123.

[21] (a) Baceiredo, A.; Bertrand, G.; Majoral, J. P. *Nouv. J. Chim.* **1983**, *7*, 255. (b) Baceiredo, A.; Bertrand, G.; Majoral, J. P.; El Anba, F.; Manuel, G. *J. Am. Chem. Soc.* **1985**, *107*, 3945. (c) Harger, M. J. P. *J. Chem. Soc., Chem. Commun.* **1971**, 442. (d) Harger, M. J. P. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2604. (e) Wiseman, J.; Westheimer, F. H. *J. Am. Chem. Soc.* **1974**, *96*, 4262. (f) Harger, M. J. P.; Stephen, M. A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 736. (g) Harger, M. J. P.; Westlake, S. *J. Chem. Soc., Perkin Trans. 1* **1981**, 3284. (h) Harger, M. J. P.; Westlake, S. *Tetrahedron* **1982**, *38*, 1511. (i) Breslow, R.; Feiring, A.; Herman, F. *J. Am. Chem. Soc.* **1974**, *96*, 5937. (j) Breslow, R.; Herman, F.; Schwabacher, A. W. *J. Am. Chem. Soc.* **1984**, *106*, 5359.

[22] Baceiredo, A.; Bertrand, G.; Mazerolles, P.; Majoral, J. P. *J. Chem. Soc., Chem. Commun.* **1981**, 1197.

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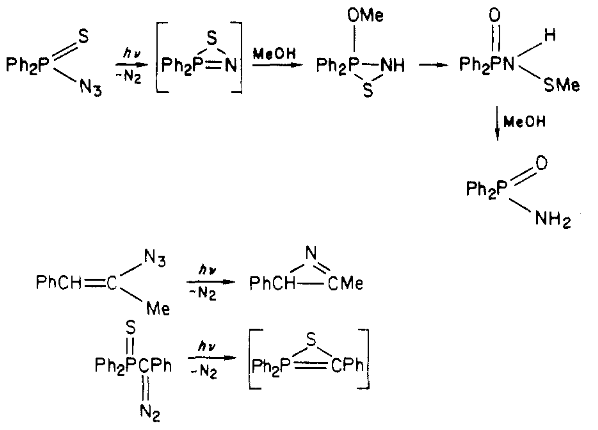
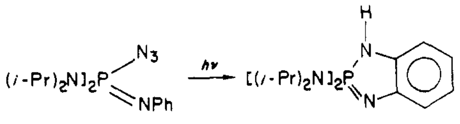
Scheme III



However, the quantitative formation of the aminodiphenylphosphine oxide in the photolysis of azidodiphenylphosphine sulfide in the presence of methanol[21a] probably involves a third type of reaction that would be similar to that observed with vinyl azides in the carbon series (Scheme III).[24]

It may be noted that the formation of an unsaturated three-membered ring has also been postulated in the case of α-thiophosphorylcarbene,[25] arguing that this behavior is not exceptional.

It is obvious that the Curtius-type rearrangement is of interest for preparing new oxoimino-, and iminothio-, and diiminophosphoranes, but the ability of phosphorus nitrenes to insert into carbon–hydrogen bonds may also be of use in the synthesis of new phosphorus heterocycles. For example, irradiation of iminophosphine azide **6** leads to a five-membered ring derivative possessing an intracyclic phosphorus–nitrogen double bond (eq 19),[21b] a type of compound that is quite rare.



(19)

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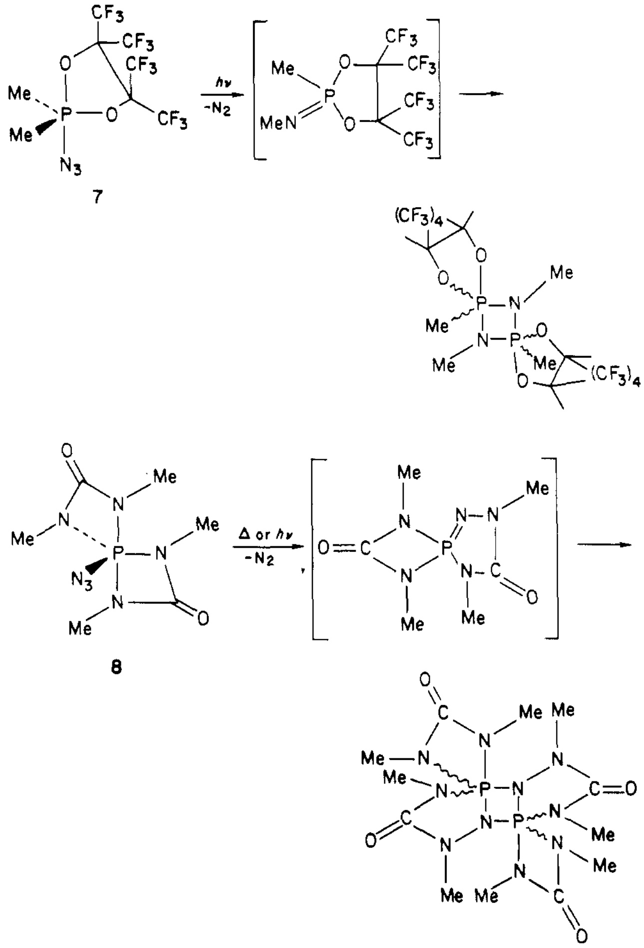
Pentacoordinated Phosphorus Azides. The very rare examples of phosphorane azides known were synthesized by an exchange reaction involving the corresponding chlorophosphorane and azidotrimethylsilane.[26,27] In fact, the scarcity of this type of compound is due to the difficulty of synthesizing the starting chlorophosphoranes.

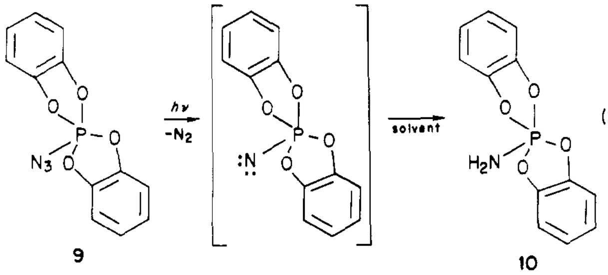
Depending on the nature of the phosphorus substituents, three different types of reaction were observed,[27] all of them involving nitrogen loss. Curtius-type rearrangements took place with azides **7** and **8**. Indeed, the formation of diazadiphosphetidine rings strongly suggests the head-to-tail dimerization of transient tetracoordinated species resulting from the migration of a phosphorus substituent to a nitrogen atom (Scheme IV).

Scheme IV



The ring-expansion reaction observed with compound **8** leads to a transient λ^4-phosphorus derivative possessing an intracyclic phosphorus–nitrogen double bond, a type of derivative that is quite rare as previously noted.

Irradiation of the pentacoordinated pentavalent phosphorus azide **9** possessing four alkoxy substituents gives aminophosphorane **10**, most probably through hydrogen abstraction from the solvent by a transient λ^5-phosphorus nitrene (eq 20). Once more, no alkoxy migration occurs because of the high thermodynamic stability of the phosphorus–oxygen bond.



(20)

9 10

The third type of rearrangement observed is due to the tendency of phosphorus derivatives to give phosphoryl species. With compound **11**, we did not obtain the expected products, resulting from either ring expansion or phenyl migration, but isocyanate **12**. Thus, there is an equilibrium between the phosphorane azide **11** and its acyclic tautomeric acyl azide that quickly rearranges via a "normal" Curtius rearrangement (Scheme V).

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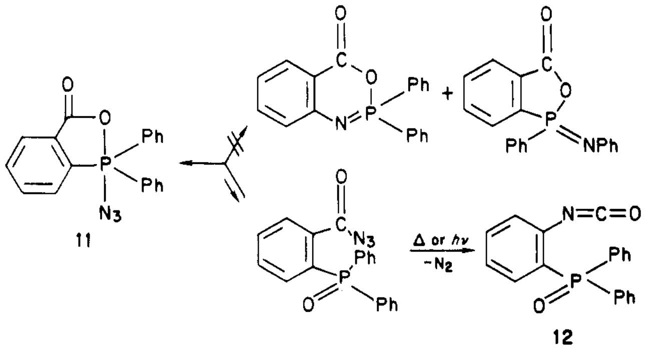
(24) Hassner, A.; Fowler, F. W. *Tetrahedron Lett.* **1967**, 1545.

(25) Yoshifuji, M.; Tagana, J.; Inamoto, N. *Tetrahedron Lett.* **1979**, 2415.

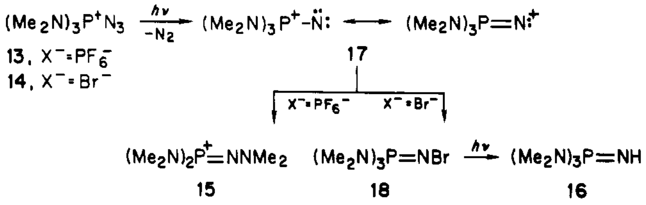
(26) Volkholz, M.; Stelzer, O.; Schmutzler, R. *Chem. Ber.* **1978**, *111*, 890.

(27) Baceiredo, A.; Bertrand, G.; Majoral, J. P.; Wermuth, U.; Schmutzler, R. *J. Am. Chem. Soc.* **1984**, *106*, 7065. Majoral, J. P.; Bertrand, G.; Baceiredo, A.; Mulliez, M.; Schmutzler, R. *Phosphorus Sulfur* **1983**, *18*, 221.

Scheme V

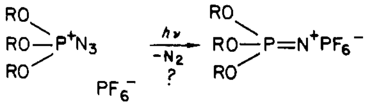


Scheme VI



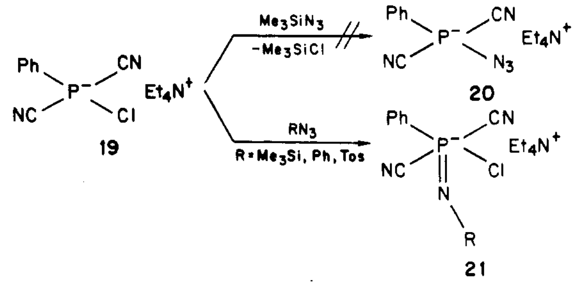
Since phosphoranes can also be in equilibrium with the corresponding phosphonium salts, we looked at the photochemical behavior of λ^5-phosphorus azides possessing a substituent linked by a bond with varying ionic character. Irradiation of tris(dimethylamino)azidophosphonium hexafluorophosphate (**13**) and bromide (**14**) gives rise to iminophosphonium salt **15** and iminophosphorane **16**, respectively.[28] The dramatic change in the course of the photolytic reaction due to the nature of the anion can be rationalized by the transient existence of a "phosphonium nitrene" in resonance with a "phosphonitrenium salt". When the anion is a poor nucleophile such as PF_6^-, the intermediate, **17**, is stabilized by migration of a phosphorus substituent onto the nitrogen atom with formation of the unusually hybridized phosphorus cation **15**.[29] On the other hand, the good nucleophilicity of the bromine anion leads to the formation of derivative **18** containing a halogen–nitrogen bond. This type of compound is very photolabile, and on subsequent irradiation in acetonitrile, **18** is converted into the iminophosphorane **16** (Scheme VI).

In contrast with alkyl- and arylnitrene, some aminonitrenes (diazenes)[30] are stable for days at −78 °C: the double-bond character of the nitrogen–nitrogen bond explains the stability of the nitrene species. Thus, one could hope to isolate a phosphonium nitrene with nonmigrating substituents and a poorly nucleophilic anion (eq 21). As yet, however, preliminary attempts to prepare the trialkoxyphosphonium azide have failed.



(21)

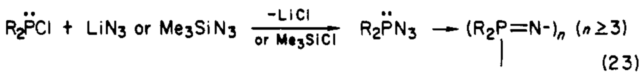
Similarly, the synthesis of phosphoranide azide **20** appears to be extremely difficult. Indeed, the expected exchange reaction of trimethylsilyl azide with the chlorophosphoranide **19** does not occur, but as for phenyl or tosyl azide, formation of the corresponding iminophosphoranure **21** (eq 22)[31] is observed. This is the first example of a Staudinger-type reaction involving a phosphorus anion.



(22)

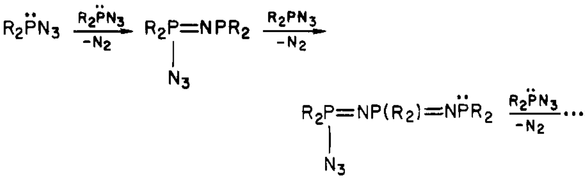
Tricoordinated Trivalent Phosphorus Azides. It is important to point out that phosphine azides constitute one of the most dangerous classes of azides. For example, diphenylphosphine azide explodes when it is banged or jarred at above −13 °C[32] and bis(trifluoromethyl)azidophosphine is a violent detonator even at the temperature of liquid nitrogen.[33]

However, these derivatives, prepared in situ, have been used to synthesize a variety of cyclo- and polyphosphazenes (eq 23).[32-34] Earlier work had led to the



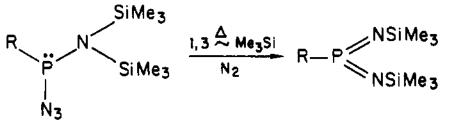
$$R_2\ddot{P}Cl + LiN_3 \text{ or } Me_3SiN_3 \xrightarrow[\text{or } Me_3SiCl]{-LiCl} R_2\ddot{P}N_3 \longrightarrow (R_2P{=}N\text{-})_n \ (n \geq 3) \quad (23)$$

belief that the formation of these polymers involves a Staudinger reaction (eq 24).[35] However, an alternative mechanism involving a transient phosphonitrile cannot be totally ruled out (see below).[35]



$$R_2\ddot{P}N_3 \xrightarrow[-N_2]{R_2\ddot{P}N_3} R_2P(N_3){=}NPR_2 \xrightarrow[-N_2]{R_2PN_3} R_2P(N_3){=}NP(R_2){=}N\ddot{P}R_2 \xrightarrow[-N_2]{R_2\ddot{P}N_3} \cdots \quad (24)$$

More recently, independent works by Niecke[36] and Nielson[37] have shown that the use of a bulky silylated amino substituent prevents intermolecular processes by masking the phosphorus lone pair. Thermolysis of these compounds provides an interesting route to stable tricoordinated pentavalent phosphorus derivatives by 1,3-migration of a trimethylsilyl group (eq 25).



(25)

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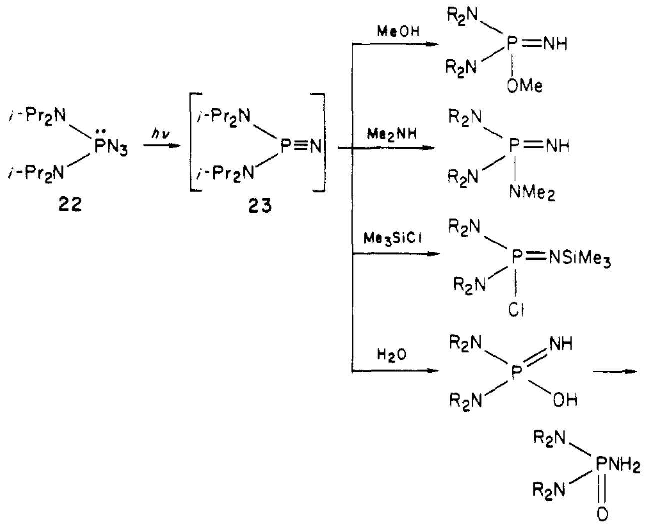
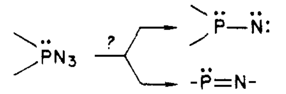
[37] Neilson, R. H. *Inorg. Chem.* **1981**, *20*, 1679. Min Xie, Z.; Neilson, R. H. *Organometallics* **1983**, *2*, 921.

Scheme VII



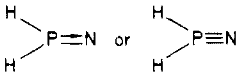
It was therefore tempting to investigate the photochemical behavior of phosphine azides bearing bulky and poorly migrating groups in order to avoid both the previous reactions and in the hope of obtaining either a Curtius-type rearrangement (eq 27) or a relatively stable phosphinonitrene (eq 26).



(26)

(27)

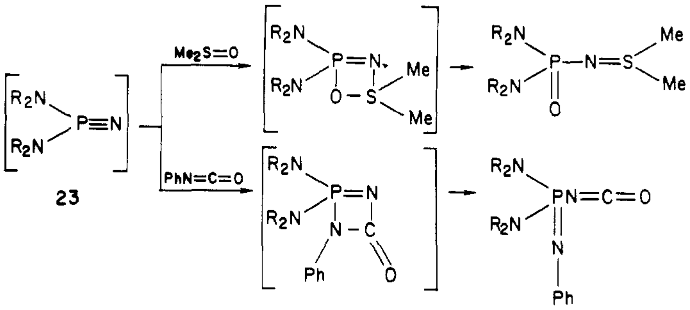
Several ab initio calculations on the structure and stabilities of H_2PN and HP=NH species have been performed.[38–41] The iminophosphane form lies about 40 kcal/mol above the phosphinonitrene. However, Hegarty et al.[38] found the energy barrier for the 1,2-hydrogen shift to be 46.5 and 30.2 kcal/mol in the singlet and triplet states, respectively, which could be large enough to guarantee the existence of stable H_2PN species. It is also interesting to note that a singlet phosphinonitrene would be about 6 kcal/mol[38,39] more stable that the triplet form mainly because of the delocalization of the lone pairs n_π (P) → p_π (N) and n_π (N) → d_π (P). In fact, the phosphorus–nitrogen bond would be best formulated as a dative double bond or a polarized triple bond, leading Trinquier[39] to name a singlet phosphinonitrene, a phosphonitrile.



The photolysis behavior of the thermally stable bis(diisopropylamino)phosphine azide **22** (prepared some years ago by Scherer et al.)[42] corroborates the theoretical predictions.

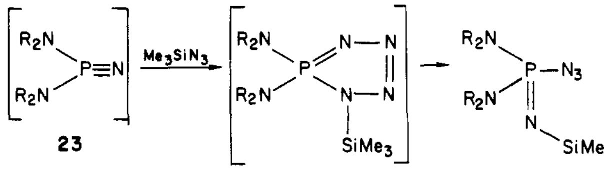
Depending on the nature of the trapping agent used, three types of reaction involving a transient phosphonitrile **23** have already been observed.[21b,43,44] With methanol, dimethylamine, trimethylchlorosilane, or water there is 1,2-addition on the phosphorus–nitrogen multiple bond (Scheme VII).

Scheme VIII



A [2 + 2] cycloaddition reaction, followed by opening of the resulting four-membered ring, explains the structure of the products obtained with phenyl isocyanate or dimethyl sulfoxide (Scheme VIII).

Lastly a [2 + 3] cycloaddition is probably involved in the case of trimethylsilyl azide. However, a Staudinger reaction with the starting phosphine azide **22** cannot be ruled out (eq 28). It may be noted that the

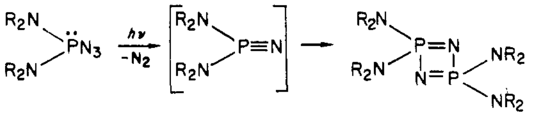


(28)

transient existence of the "phosphinonitrene–phosphonitrile" intermediate **23** has been confirmed by ^{31}P NMR[21b] ($\delta(^{31}P) = +246$) and photoelectron[45] spectroscopy.

Specific nitrene-trapping agents such as monoolefins, conjugated dienes, or dimethyl sulfide do not react with this intermediate. Moreover, we never observed the formation of a product involving a triplet phosphinonitrene such as $[(i\text{-Pr})_2N]_2PNH_2$, which would have resulted from hydrogen-abstraction reaction from the solvent.

Unambiguous proof for the multiple-bond character of the phosphinonitrene **23** has been found in the characterization of the first stable cyclodiphosphazene **24**[21b,46]–namely 2,2,4,4-tetrakis(diisopropylamino)-1,3,2λ^5,4λ^5-diazadiphosphete—which is obviously the dimer of a phosphonitrile (eq 29).



(29)

The structure of the four-membered ring has been clearly established by a single-crystal X-ray diffraction study.[46] Its surprising stability is probably due to the high thermodynamic energy of the corresponding monomer, preventing dissociation, and to steric factors that hinder polymerization. Indeed, according to recent theoretical calculations,[47,48] the cyclodimerization of two

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(38) Nguyen, M. T.; McGinn, M. A.; Hegarty, A. F., submitted for publication in *J. Am. Chem. Soc.*

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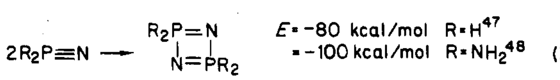
(45) Gonbeau, D.; Pfister-Guillouzo, G., private communication.

(46) Baceiredo, A.; Bertrand, G.; Majoral, J. P.; Sicard, G.; Jaud, J.; Galy, J. *J. Am. Chem. Soc.* **1984**, *106*, 6088.

(47) Trinquier, G., submitted for publication in *J. Am. Chem. Soc.*

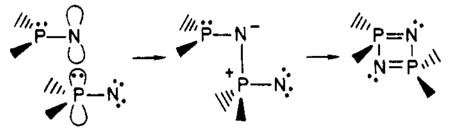
(48) Ahlrichs, R.; Schiffer, H., submitted for publication in *J. Am. Chem. Soc.*

$R_2P{\equiv}N$ units results in a large energy benefit especially with amino substituents (eq 30).



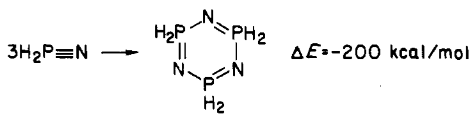
(30)

For a direct least motion concerted pathway, this reaction is quasi-forbidden thermally but is photochemically allowed when starting from R_2PN units in a $\pi \rightarrow \pi^*$ (i.e., n_π (P) $\rightarrow \pi$(N)) excited state. The experimental results can be easily explained since the *phosphinonitrene is generated by UV irradiation or* because an alternative stepwise pathway with an open zwitterionic intermediate (eq 31) is perfectly allowed thermally and probably requires a weak activation energy if any.



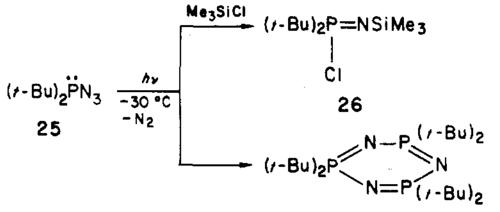
(31)

On the other hand, the trimerization reaction is even more thermodynamically favored (eq 32),[47] and kinetic factors (steric hindrance) must play the greatest part in preventing the reaction from going beyond cyclodimerization.



(32)

This has been confirmed by experimental results. Photolysis of di-*tert*-butylphosphine azide (**25**) in the presence of trimethylchlorosilane gives rise to the expected adduct **26** on the transient phosphonitrile, but in the absence of trapping agent we observed the formation of the cyclotriphosphazene **27**[49] and no evidence for the dimer was seen (eq 33).



(33)

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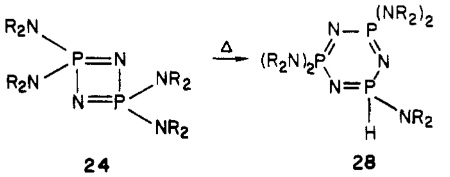
Moreover, heating of the tetrakis(diisopropylamino)cyclodiphosphazene (**24**) leads to a trimer **28** (eq 34).[49]

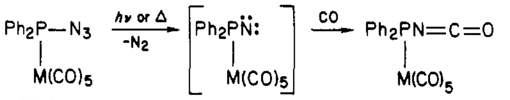


(34)

24 **28**

These results as a whole should shed new light on questions of equilibria among monomers, rings, and chains in phosphazenes. They could also be important in understanding the formation of commercial linear high polyphosphazenes.[50]

Another important point concerning phosphine azides is the absence of a 1,2-shift from the phosphorus to the nitrogen. Since all the different processes mentioned above involve the phosphorus lone pair, one might anticipate that the complexation of the phosphorus atom would encourage a Curtius-type rearrangement and thereby provide a facile route to iminophosphane complexes. In fact, irradiation of tungsten or chromium pentacarbonyl complexes of diphenylphosphine azide leads to isocyanatophosphine complexes **29**, most probably via the transient formation of a phosphinonitrene intermediate that combines with carbon monoxide (eq 35).[51]



(35)

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Concluding Remarks

It has been shown that the Curtius rearrangement is effective for group 13 (B), group 14 (C, Si, Ge), and group 15 (P) azides. Competitive nitrene-type reactions sometimes occur. When our results and those of other researchers are critically analyzed, it is clear that the rearrangement of azides tends to follow a predictable pattern:

(i) If heteroatom M, bound to the azido group, does not possess a lone pair of electrons, a Curtius-type rearrangement can occur, whereby the coordination number of M is decreased by 1 unit but the number of valence bonds is maintained (eq 36).

$$R_nMN_3 \xrightarrow[\text{or } h\nu]{\Delta} R_{n-1}M{=}NR + N_2 \qquad (36)$$

(ii) If atom M bound to the azido group has a lone pair of electrons as well as accessible d orbitals, expulsion of nitrogen can occur, but the coordination number of M remains unchanged while the number of valence bonds increases by 2 units (eq 37).

$$R_nMN_3 \xrightarrow[\text{or } h\nu]{\Delta} R_nM{\equiv}N + N_2 \qquad (37)$$

These rules should help in designing specific azide precursors for the synthesis of original "unusually hybridized" heavier main-group element species.

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(49) Ocando, E.; Majoral, J. P.; Bertrand, G., unpublished results.

(50) Allcock, H. R. *Chem. Eng. News* **1985**, *63*, 22.

(51) Ocando, E.; Majid, S.; Majoral, J. P.; Baceiredo, A.; Bertrand. G. *Polyhedron* **1985**, *4*, 1667.

(52) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)