

Versatile Photochemical Behavior of Phosphorus Azides: Curtius-Type Rearrangement and Diverse Fates of α -Phosphorus Nitrenes

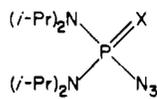
Antoine Baceiredo,[†] Guy Bertrand,^{*†} Jean-Pierre Majoral,^{*†} Fatiha El Anba,[†] and Georges Manuel[†]

Contribution from Laboratoire des Organométalliques, ERA 829, and Laboratoire de Synthèse, Réactivité et Structure de Molécules Phosphorées, ERA 926, Université Paul-Sabatier, 31062 Toulouse Cedex, France. Received November 16, 1984

Abstract: The photolytic behavior of bis(diisopropylamino)phosphine azide **1** and its oxo **2**, thio **3**, and phenylimino **4** analogues is reported. Irradiation of **1** leads to a relatively stable, singlet phosphinonitrene ($>P=N$) which reacts as a phosphonitrile ($>P=N$) **16** presenting a ^{31}P chemical shift of +246 ppm. Photolysis of **2** gives rise to a transient oxo-iminophosphorane **7** through a Curtius-type rearrangement. In the case of **3**, besides the formation of a short-lived thio-iminophosphorane **12**, compound **8** arising from hydrogen abstraction of the solvent by a thiophosphorylnitrene **11** is obtained. A cyclic phosphazene **13** coming from an intramolecular carbon-hydrogen insertion of a nitrene is characterized by irradiation of **4**.

Organic azides have received considerable attention over the years.¹ In contrast, studies concerning phosphorus azides have been mainly restricted to their use as reagents in organic synthesis² and to the generation of tricoordinated pentavalent phosphorus species.³ It is only recently that Curtius-type rearrangements involving pentacoordinated phosphorus azides⁴ and phosphonium azides⁵ have been reported.

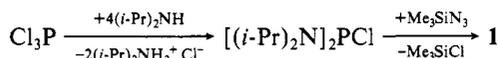
Here we wish to report that phosphorus azides can also be very powerful starting materials for the synthesis of new, unusually hybridized species and novel phosphorus heterocycles. Comparing the photolytic behavior of bis(diisopropylamino)phosphine azide **1** and its oxo **2**, thio **3**, and phenylimino **4** analogues, we show that the reaction course is extremely sensitive to the environment of the phosphorus atom.



- 1, X = lone pair
2, X = O
3, X = S
4, X = N-Ph

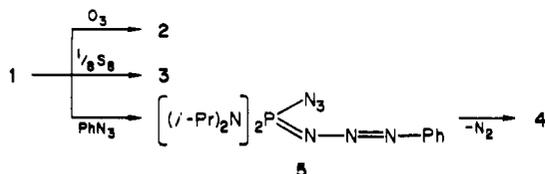
Results and Discussion

Synthesis of Phosphorus Azides. An exchange reaction of bis(diisopropylamino)phosphine chloride (directly prepared from phosphorus trichloride and diisopropylamine) with azidotrimethylsilane leads to phosphine azide **1**.



Azide **1** is not sensitive to the action of classical oxidizing agents such as dimethyl sulfoxide or hydrogen peroxide. However, the oxide of bis(diisopropylamino)phosphine azide **2** is readily available through the action of ozone on **1**. Note that only 1 mol of ozone is necessary to oxidize 2 mol of phosphine **1**.

Addition of sulfur to **1** leads to the corresponding sulfide **3** while phenyl azide gives rise to iminophosphine **4** via the spectroscopically characterized adduct **5** ($\delta^{31}P$ 33 ppm).



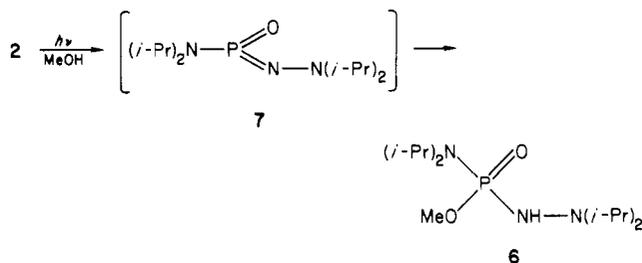
[†]Laboratoire des Organométalliques.

[‡]Laboratoire de Synthèse, Réactivité et Structure de Molécules Phosphorées.

Although up to date no explosions have occurred with these azides, maximum care must be taken.

Photolysis of Tetracoordinated Phosphorus Azides 2, 3, and 4. Photolysis of λ_5 phosphorus azides **2**, **3**, and **4** were performed in toluene solution at 254 nm and at room temperature overnight.

Irradiation of the oxide **2** in the presence of methanol as trapping agent allows the characterization of **6** in 80% isolated yield. Formation of **6** can be easily rationalized by 1,2 addition of methanol to the phosphorus-nitrogen double bond of a transient tricoordinated pentavalent phosphorus derivative **7**. Thus, we



can conclude that a Curtius-type rearrangement is involved in the photolysis of azide **2**. A similar rearrangement has already been observed for other azides of phosphine oxide.^{3a-8}

The photolysis of the sulfur analogue **3** in the presence of methanol is more complex and leads to the three products, **8**, **9**, and **10**.

Transient existence of a thiophosphonitrene **11**, followed by a hydrogen abstraction reaction from the solvent, may explain the formation of **8** although it is impossible to totally exclude a non-nitrene mechanism.^{1c}

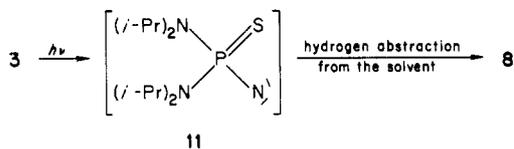
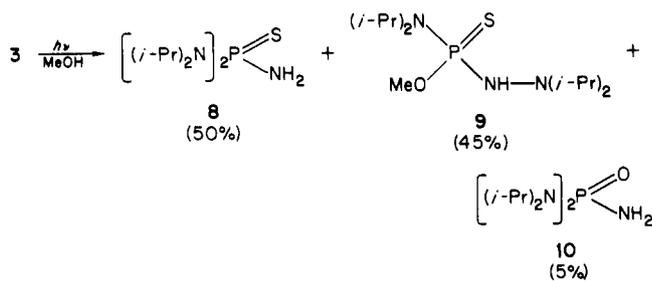
(1) (a) Curtius, Th. *Ber.* **1890**, *23*, 3023. (b) Patai, S. "The Chemistry of the Azido Group"; Wiley-Interscience: New-York, 1971. (c) Lwowski, W. "Nitrenes"; Wiley-Interscience: New-York, 1970.

(2) (a) Gololobov, Yu. G.; Zhmurova, I. N.; Kasukhin, L. F. *Tetrahedron* **1981**, *37*, 437. (b) Gilyarov, V. A. *Russ. Chem. Rev.* **1982**, *51* (9), 909. (c) Shiori, T.; Ninomiya, K.; Yamada, S. *J. Am. Chem. Soc.* **1972**, *94*, 6203. (d) Shiori, T.; Yamada, S. *Chem. Pharm. Bull.* **1974**, *22*, 849, 855, 859. (e) Vaultier, M.; Knouzi, N.; Carrié, R. *Tetrahedron Lett.* **1983**, *24*, 763.

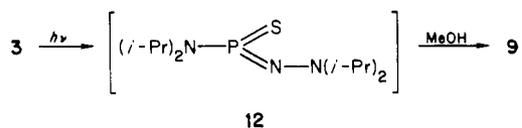
(3) (a) Bertrand, G.; Majoral, J. P.; Baceiredo, A. *Tetrahedron Lett.* **1980**, *21*, 5015. (b) Baceiredo, A.; Bertrand, G.; Majoral, J. P. *Nouv. J. Chim.* **1983**, *7*, 255. (c) Wiseman, J.; Westheimer, F. H. *J. Am. Chem. Soc.* **1974**, *96*, 4262. (d) Breslow, R.; Feiring, A.; Herman, F. *Ibid.* **1974**, *96*, 5937. (e) Harger, M. J. P.; Stephen, M. A. *J. Chem. Soc. Perkin Trans. 1* **1981**, 736. (f) Harger, M. J. P.; Westlake, S. *Tetrahedron* **1982**, *38*, 1511. (g) Harger, M. J. P.; Westlake, S. *Tetrahedron Lett.* **1982**, *23*, 3621. (h) Min Xie, Z.; Nielson, R. H. *Organometallics*, **1983**, *2*, 921. (i) Schäfer, H. G. Dissertation, Universität Bielefeld, 1981. (j) Wildbredt, D. A. Dissertation, Universität Bielefeld, 1981.

(4) Baceiredo, A.; Bertrand, G.; Majoral, J. P.; Wermuth, U.; Schmutzler, R. *J. Am. Chem. Soc.* **1984**, *106*, 7065.

(5) Mulliez, M.; Majoral, J. P.; Bertrand, G. *J. Chem. Soc., Chem. Commun.* **1984**, 284.

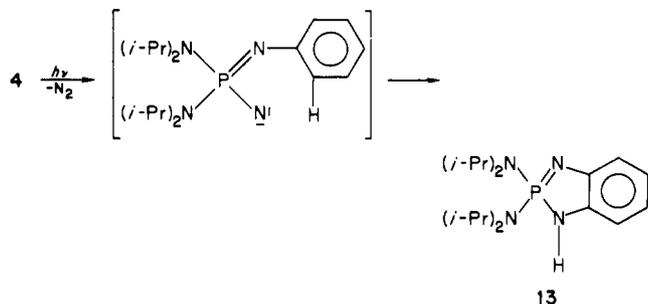


Addition of methanol to a thio-iminophosphorane intermediate **11** is almost certainly responsible for the formation of derivative **9**. This is the first example of a Curtius-type rearrangement involving an azido λ^5 phosphorus sulfide. The mechanism of the



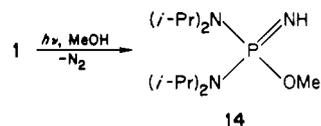
reaction leading to **10** is still uncertain, but since this product was only observed in a very low yield (<5%), a mechanistic hypothesis is not of great interest.

The photolytic behavior of bis(diisopropylamino)phenyl-iminophosphine azide **4** is entirely different from that previously observed for derivatives **2** and **3**. Irradiation of **4** in the presence or in the absence of methanol gives the cyclic phosphazene derivative **13**, most probably through a nitrene insertion into a carbon-hydrogen bond of the phenyl substituent. Note that, here also, it is impossible to exclude a non-nitrene mechanism.

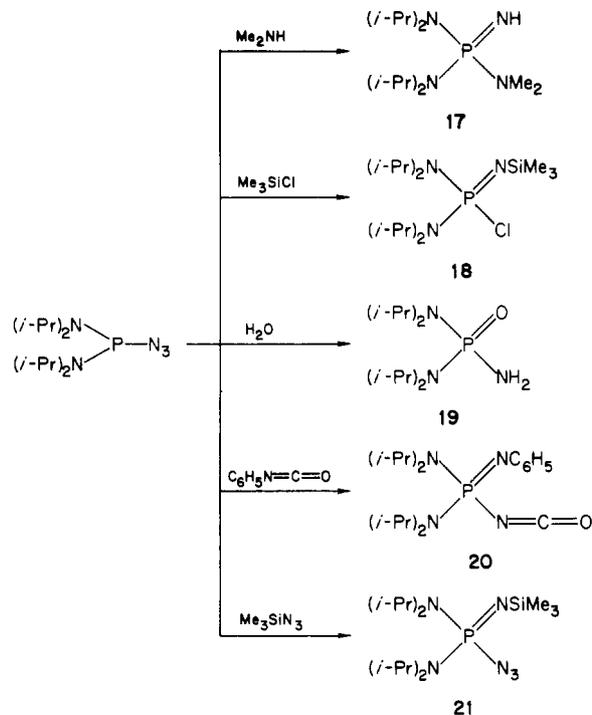


Although in carbon^{1c} and in silicon chemistry⁷ intramolecular nitrene insertion is a known reaction, to our knowledge this is the first example of such an intramolecular reaction in phosphorus chemistry. It is noteworthy that only a few stable cyclic five-membered rings with a phosphorus(V)-nitrogen double bond are known.⁸

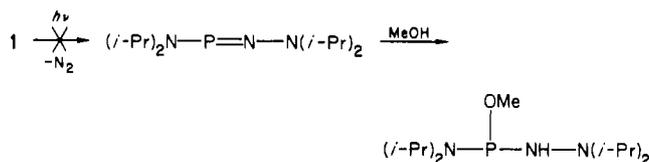
Photolysis of Bis(diisopropylamino)phosphine Azide 1.⁹ Irradiation of phosphine azide **1**, in benzene solution, at 254 or 300 nm at room temperature for 6 h in the presence of a stoichiometric amount of methanol affords the phosphazene **14** quantitatively.



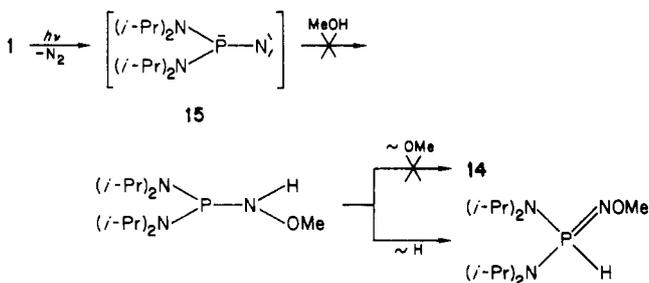
Scheme I. Photolysis of Bis(diisopropylamino)phosphine azide **1** in the Presence of Various Trapping Agents



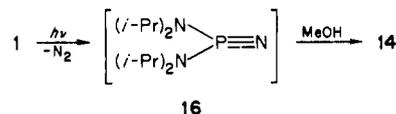
Since two diisopropylamino groups remain on the phosphorus atom, it is obvious that no Curtius-type rearrangement occurs.



On the other hand, it is not likely that derivative **14** arises from the insertion of a phosphinonitrene **15** into a hydrogen-oxygen bond of methanol^{3e} followed by a methoxy group migration since 1,2-hydrogen shift would be much more favorable.¹⁰



The most plausible explanation for the formation of phosphazene **14** is a 1,2 addition of methanol to a phosphorus-nitrogen triple-bonded intermediate **16** obtained by loss of nitrogen from **1**.



This hypothesis is corroborated by ab initio calculations¹¹ which postulate that a singlet phosphinonitrene can be formulated to

(6) (a) Banks, R. E.; Berry, D.; McGlinchey, M. J. *J. Chem. Soc. C* **1970**, 1017. (b) Pancrazi, A.; Khuong-Huu, Q. *Tetrahedron* **1975**, *31*, 2041.

(7) Gaidis, J. M.; West, R. J. *Am. Chem. Soc.* **1964**, *86*, 5699.

(8) Schmidpeter, A.; Nayibi, M.; Mayer, P.; Tautz, H. *Chem. Ber.* **1983**, *116*, 1468. Schmidpeter, A.; Von Griegern, T. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 55.

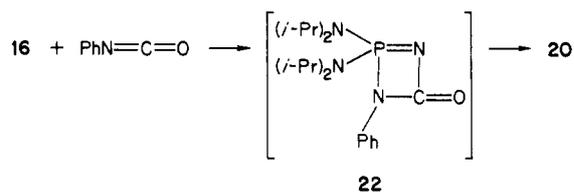
(9) For preliminary account of this work, see: Sicard, G.; Baceiredo, A.; Bertrand, G.; Majoral, J. P. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 459.

(10) (a) Schmidpeter, A.; Rosknecht, H. *Z. Naturforsch., Teil B* **1971**, *26*, 2, 81. (b) Binder, H.; Fisher, R. *Chem. Ber.* **1974**, *107*, 205. (c) O'Neal, H. R.; Neilson, R. H. *Inorg. Chem.* **1984**, *23*, 1372.

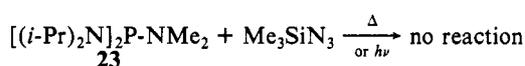
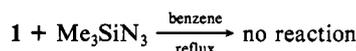
(11) Trinquier, G. *J. Am. Chem. Soc.* **1982**, *104*, 6969.

a certain extent as a phosphonitrile owing to delocalization of the lone pairs $n_r(\text{P}) \rightarrow p_r(\text{N})$ and $n_r(\text{N}) \rightarrow d_r(\text{P})$. Moreover, although most nitrenes have triplet ground state,¹² the theoretical approach performed on the parent compound (H_2PN) showed that the phosphonitrile has a singlet ground state with a singlet-triplet separation calculated at the CI level to be 6 kcal/mol.¹¹

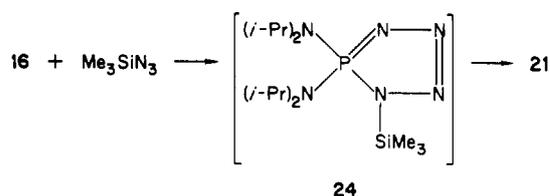
The transient existence of phosphonitrile **16** has been further demonstrated by other trapping reactions (Scheme I). Dimethylamine, trimethylchlorosilane, and water, like methanol, give quantitative 1,2 addition on the phosphorus–nitrogen triple bond of phosphonitrile **16**. In the case of water, a subsequent hydroxyimino-oxoamino rearrangement explains the formation of the amino bis(diisopropylamino)phosphine oxide **19**. The diamino(imino)isocyanato λ^5 phosphine **20** probably arises from [2 + 2] cycloaddition of phenyl isocyanate to **16** followed by ring opening of the resulting strained cyclic adduct **22**.



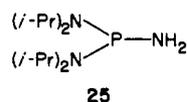
The iminophosphine azide **21** formally results from a Staudinger reaction involving the starting phosphine azide **1**. However, (i) the Staudinger reactions are usually thermally and not photochemically induced,^{2a} and, in the absence of irradiation, even in refluxing benzene, trimethylsilyl azide does not react with phosphine **1**. (ii) No reaction occurs by heating or irradiating the bis(diisopropylamino)dimethylaminophosphine **23** in the presence of Me_3SiN_3 .



Thus, two possibilities can explain the formation of adduct **21**: an insertion reaction of phosphonitrile **16** into the silicon–nitrogen σ bond of the silyl azide or, much more likely, a [2 + 3] cycloaddition followed by ring opening of the resulting phosphatetrazole derivative **24**.



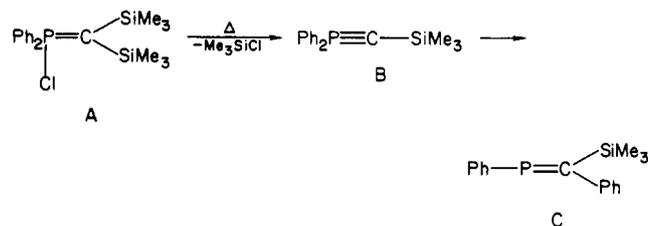
It is of interest to note that no trapping reactions occurred when specific nitrene trapping agents such as monoolefins, conjugated dienes, or dimethyl sulfide were used. Moreover, we never observed the formation of amine **25** which would have resulted from



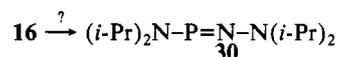
a hydrogen abstraction reaction from the solvent by a triplet phosphonitrile **15**.

At this stage, we can conclude that the photolysis of bis(diisopropylamino)phosphine azide **1** leads to a transient, singlet phosphonitrile which reacts as a phosphonitrile **16** with a strongly polarized phosphorus–nitrogen triple bond. A question remained;

what would be the fate of phosphonitrile **16** in the absence of any trapping agent? The only result concerning a λ^5 phosphorus triple-bonded compound was reported by Appel et al.¹³ who postulated the transient existence of a λ^5 phosphaacetylene **B** to explain the formation of the phosphalkene **C** in the thermolysis of derivative **A**. Thus, one could imagine that phosphonitrile **16**

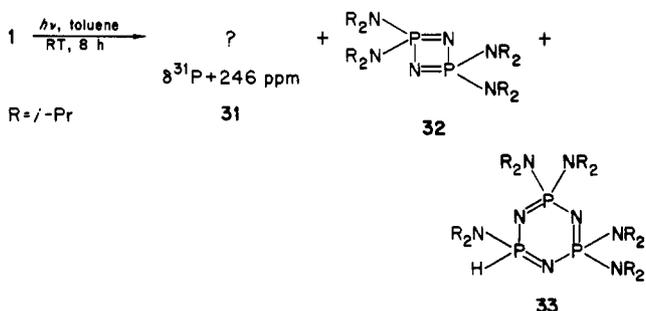


would rearrange to give a dicoordinated phosphorus derivative **30**.



Note that this hypothesis is not in disagreement with the results observed in the cophotolysis of azide **1** with trapping agents since the lifetime of **16** could be sufficient to allow trapping reactions. However, although dicoordinated phosphorus derivative **30** should be much lower in energy than phosphonitrile **16**,¹¹ one must keep in mind that significant energy barriers may exist for the 1,2 shifts, and thus the singlet phosphonitrile **16** should prefer polymolecular reactivity.

When azide **1** was irradiated in toluene solution at 300 nm and room temperature 8 h, three products were detected by ³¹P NMR spectroscopy. One of the signals ($\delta^{31}\text{P}\{^1\text{H}\} +246$ ppm, s, 6% relative integration) disappeared after a few hours. After workup, the other derivatives **32** ($\delta^{31}\text{P}\{^1\text{H}\} +40$ ppm, s) and **33** ($\delta^{31}\text{P}\{^1\text{H}\} +20$ ppm, d, and -4 ppm, t, $J_{\text{pp}} = 38$ Hz) were isolated in 42 and 3% yield, respectively.



The cyclodiphosphazene structure **32** has been clearly established by a single X-ray diffraction study.¹⁴ The surprising stability of **32**, which is the first heterocyclobutadiene to be isolated (non-air-sensitive, white crystals, mp 110 °C without decomposition) is probably due to the high thermodynamic energy of the corresponding monomer preventing dissociation; parent cyclodiphosphazene ($\text{H}_2\text{P}=\text{N}-$)₂ is predicted by ab initio calculations¹⁵ to be 80 kcal more stable than two molecules of phosphonitrile $\text{H}_2\text{P}=\text{N}$ and to steric factors which hinder polymolecular reactivity.

Obviously, the formation of this unsaturated four-membered ring **32** results from head-to-tail dimerization of phosphonitrile **16**.

Minor compound **33** was characterized as the first hydrido-pentaaminocyclotriphosphazene. Only a few examples of hydridocyclotriphosphazenes are known.¹⁶ The six-membered ring

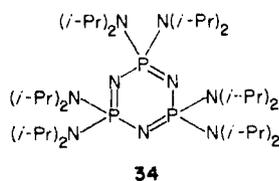
(12) (a) Davidson, E. R. "Diradicals"; Borden, W. T., Ed.; Wiley: New York, 1982; p 73. (b) Drzaic, P. S.; Brauman, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 3443. (c) Huber, K. R.; Herzberg, G. "Constants of Diatomic Molecules"; Van Nostrand-Reinhold: New York, 1979. (d) Demuynck, J.; Fox, D. J.; Yamaguchi, Y.; Schaefer, H. F. III *J. Am. Chem. Soc.* **1980**, *102*, 6204.

(13) Appel, R.; Barth, V.; Peters, J. *Int. Conf. Phosphorus Chem., Halle 1979*. Appel, R.; Peters, J.; Schmitz, R. *Z. Anorg. Allg. Chem.* **1981**, *475*, 18.

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

(15) Trinquier, G.; Daudey, J. P.; Bertrand, G.; Majoral, J. P., unpublished results.

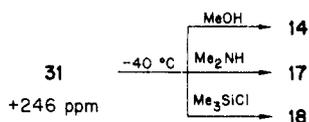
33 is thermally and photochemically stable, not sensitive to water or air exposure, and can be isolated by liquid chromatography. It is noteworthy that no traces of hexaaminocyclotriphosphazene **34** were detected.



Irradiation of azide **1** in deuterated benzene also leads to hydrogenocyclotriphosphazene **33**, excluding its formation through a homolytic cleavage of an exocyclic phosphorus–nitrogen bond of **34** followed by hydrogen abstraction from the solvent; therefore, the hydrogen atom comes from a diisopropylamino group. Although, the mechanism of the reaction leading to cyclotriphosphazene **33** is still debatable, we can conclude that, surprisingly, phosphonitrile **16** prefers to dimerize, under photolytic conditions, rather than to trimerize.

Concerning product **31**, in a first approach, its ^{31}P chemical shift is in good agreement¹⁷ with that expected for the dicoordinated phosphorus derivative **30**, which would be obtained via a Curtius-type rearrangement. Nevertheless, such a species would be very unstable and would quickly dimerize, at room temperature into the corresponding diazadiphosphetidine.¹⁸ In our case, no trace of a dimer of this type has ever been detected. In fact, no new signals have been observed after complete disappearance of the signal at +246 ppm. 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 derivative has yet been spectroscopically characterized.

To tentatively assign this signal, methanol, dimethylamine, or chlorotrimethylsilane was added at -40°C to the photochemical reaction mixture obtained after 2 h of irradiation at -40°C . Beside the signals corresponding to the starting azide **1** and cyclodiphosphazene **32**, the singlets corresponding to the expected adducts of the phosphonitrile **16** were clearly observed.¹⁹ Thus



it seems quite likely that phosphonitrile **16** = **31** presents a ^{31}P chemical shift of +246 ppm, has a half-lifetime of about 12 h at room temperature, and is stable for several days at -40°C . Its dimerization is favored by UV irradiation.

The relative stability of bis(diisopropylamino)phosphonitrile **16** is not really astonishing since Dervan et al.²⁰ reported that, in contrast with the other types of nitrenes,^{21,22} aminonitrenes

(16) For examples, see: (a) Allcock, H. R.; Scopelianos, A. G.; Wittle, R. R.; Tollefson, N. M. *J. Am. Chem. Soc.* **1983**, *105*, 1316. (b) Ritchie, R. J.; Harris, P. J.; Allcock, H. R. *Inorg. Chem.* **1983**, *19*, 2483. (c) Harris, P. J.; Allcock, H. R. *J. Am. Chem. Soc.* **1978**, *100*, 6512. (d) Allcock, H. R.; Harris, P. J. *Ibid.* **1979**, *101*, 6221. (e) Schmidpeter, A.; Ebeling, J.; Stary, H.; Weingrand, C. *Z. Anorg. Chem.* **1972**, *394*, 171. (f) Bermaun, A.; Van Wazer, J. R. *Inorg. Chem.* **1972**, *11*, 209.

(17) Fluck, E. *Top. Phosphorus Chem.* **1980**, *10*, 193.

(18) Niecke, E.; Flick, W.; Pohl, S. *Angew. Chem.* **1976**, *88*, 305; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 309.

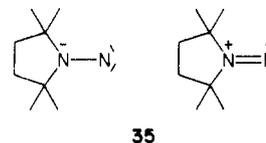
(19) Taking into account the small amount of phosphonitrile **31**, isolation of the adducts was impossible. Nevertheless, their characterization were performed by ^1H and ^{31}P Co-NMR with authentic samples.

(20) (a) Hinsberg, W. D.; Dervan, P. B. *J. Am. Chem. Soc.*, **1978**, *100*, 1608. (b) Hinsberg, W. D.; Dervan, P. B. *Ibid.* **1979**, *101*, 6142. (c) Schultz, P. G.; Dervan, P. B. *Ibid.* **1980**, *102*, 878. (d) Dervan, P. B.; Squillacote, M.; Lahti, P.; Sylwester, A. P.; Roberts, J. D. *Ibid.* **1981**, *103*, 1120. (e) Schultz, P. G.; Dervan, P. B. *Ibid.* **1981**, *103*, 1563. (f) Hinsberg, W. D.; Schultz, P. G.; Dervan, P. B. *Ibid.* **1982**, *104*, 766. (g) McIntyre, D. K.; Dervan, P. B. *Ibid.* **1982**, *104*, 6466. (h) Schultz, P. G.; Dervan, P. B. *Ibid.* **1982**, *104*, 6660.

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

(22) Lwowski, W. "Reactive Intermediates", Jones, M., Moss, R., Eds.; Wiley: New York, 1978; Chapter 6.

(diazenes) such as **35** are stable for days at -78°C : the multiple character of the nitrogen–nitrogen bond explains the stabilization of the nitrene species.



Experimental Section

All experiments were performed in an atmosphere of dry argon or nitrogen. Melting points are uncorrected. ^1H NMR spectra were recorded on a Varian T-60 or Bruker WM 250 spectrometer. ^1H chemical shifts are reported in ppm relative to Me_4Si as internal standard. ^{31}P NMR spectra were obtained on a Perkin-Elmer R32 spectrometer at 36.4 MHz or Bruker WM 250 at 101.21 MHz. Downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4 . ^{13}C NMR spectra were recorded on Bruker WM 250 at 62.86 MHz. Infrared spectra were recorded on a Beckman IR 10 spectrometer, using polystyrene film for calibration. Mass spectra were obtained on a Ribermerg R10-10E instrument.

Photochemical reactions were performed in quartz tubes, using a Rayonet photochemical reactor. Preparative liquid chromatography was carried out on Merck, Kieselgel 60, 230–400 mesh ASTM.

Synthesis of the Phosphine Azide 1.²³ Trimethylsilyl azide (8 g, 0.07 mol) was added to a solution of bis(diisopropylamino)chlorophosphine^{23,24} (10 g, 0.0375 mol) in 15 mL of benzene. The solution was stirred for 2 days at room temperature. First the solvent and then excess silyl azide was removed at reduced pressure (15 mm). The residue was either dissolved in hot acetonitrile and the solution cooled to -30°C , causing precipitation of **1** (5.12 g, 50%) as white crystals (mp $37\text{--}39^\circ\text{C}$), or distilled as a colorless liquid that crystallized on standing (bp 80°C (0.1 mmHg, 7.17 g, 70%): ^{31}P NMR (C_6H_6) +105 ppm (s); ^1H NMR (CDCl_3); 1.12 (d, $J(\text{HH}) = 7$ Hz, 12 H, CH_3), 1.18 (d, $J(\text{HH}) = 7$ Hz, 12 H, CH_3), 3.40 (sept-like, $J(\text{HH}) = 7$ Hz, 4 H, CH); ^{13}C NMR [^1H] (CDCl_3) 23.85, 23.94, 24.03, and 24.17 (s, CH_3), 45.93 and 46.14 (s, CH); IR (KBr) 2100 cm^{-1} (P–N₃). Anal. Calcd for $\text{C}_{12}\text{H}_{28}\text{N}_3\text{P}$: C, 52.72; H, 10.32; N, 25.62. Found: C, 52.85; H, 10.36; N, 25.58.

Synthesis of the Azidobis(diisopropylamino)phosphine Oxide (2). Three liters of the mixture O_2/O_3 (2 mmol of ozone) was bubbled through a solution of phosphine **1** (1 g, 3.6 mmol) in anhydrous toluene at -78°C . The phosphine oxide **2** was isolated by liquid chromatography (ether/petroleum ether 40/60, R_f 0.64) as white crystals (0.94 g, 90%, mp 44°C): ^{31}P NMR (toluene) +14.5 (s); ^1H NMR (CDCl_3) 1.24 (d, $J(\text{HH}) = 7$ Hz, 12 H, CH_3), 1.27 (d, $J(\text{HH}) = 7$ Hz, 12 H, CH_3), 3.45 (d of sept, $J(\text{HH}) = 7$ Hz, $J_{\text{P-H}} < 0.3$ Hz, 4 H, CH); IR (KBr) 2150 (P–N₃), 1240 (P=O), 1000 (P–N) cm^{-1} ; mass spectrum m/e 289 (M^+) 273, 189. Anal. Calcd for $\text{C}_{12}\text{H}_{28}\text{N}_3\text{OP}$: C, 49.80; H, 9.75; N, 24.20. Found: C, 49.75; H, 9.76; N, 24.22.

Synthesis of the Azidobis(diisopropylamino)phosphine Sulfide (3). A solution of phosphine **1** (1.5 g, 5.49 mmol) in 5 mL of anhydrous dichloromethane and sulfur (0.2 g) was stirred for 1 h at room temperature. Excess of sulfur was filtered and solvent was removed from the filtrate under reduced pressure. The residue was purified by liquid chromatography (ether/petroleum ether 50/50, R_f 0.46). Removal of solvents gave **3** as white crystals (1.29 g, 77%, mp 85°C): ^{31}P NMR (CDCl_3) +62.9 (s); ^1H NMR (CDCl_3) 1.25 (d, $J(\text{HH}) = 7$ Hz, 12 H, CH_3), 1.31 (d, $J(\text{HH}) = 7$ Hz, 12 H, CH_3), 3.6 (d of sept, $J(\text{HH}) = 7$ Hz, $J_{\text{P-H}} < 0.3$ Hz, 4 H, CH); IR (KBr) 2160 (P–N₃), 990 (P–N) cm^{-1} ; mass spectrum m/e 305 (M^+), 263, 205, 173. Anal. Calcd for $\text{C}_{12}\text{H}_{28}\text{N}_3\text{PS}$: C, 47.19; H, 9.24; N, 22.93. Found: C, 47.03; H, 9.22; N, 22.96.

Synthesis of the Phenyliminobis(diisopropylamino)phosphine Azide (4). Phenyl azide (1.19 g, 0.01 mol) was added to a solution of the phosphine azide **1** (2.73 g, 0.01 mol) in 20 mL of benzene. The solution was stirred for 2 h at 80°C . After evaporation of the solvent under reduced pressure, the residue was purified by liquid chromatography (ether/petroleum ether 50/50, R_f 0.5), affording **4** as white crystals (3.27 g, 90%, mp 103°C): ^{31}P NMR (C_6H_6) –8 (s); ^1H NMR (CDCl_3) 1.20 (d, $J(\text{HH}) = 7$ Hz, 24 H, CH_3), 3.53 (sept-like, $J(\text{HH}) = 7$ Hz, 4 H, CH), 6.6–7.4 (m, 5 H, H (arom)); IR (KBr) 2140 (P–N₃), 1278 (P=N–) cm^{-1} ; mass spectrum m/e 364 (M^+). Anal. Calcd for $\text{C}_{18}\text{H}_{33}\text{N}_4\text{P}$: C, 59.31; H, 9.13; N, 23.06. Found: C, 59.10; H, 9.13; N, 23.13.

Photolysis of the Azidobis(diisopropylamino)phosphine Oxide (2). A solution of **2** (0.23 g, 0.796 mmol) and methanol (0.064 g, 2 mmol) in

(23) Scherer, O. J.; Glabel, W. *Chem. Ztg.* **1975**, *99*, 246.

(24) Gynane, J. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **1980**, 2428.

6 mL of anhydrous toluene was irradiated at 254 nm for 18 h at -40°C . After removal of the solvent at reduced pressure (15 mm), **6** was isolated by liquid chromatography (methanol/ether 1/99, R_f 0.5) as white crystals (0.186 g, 80%, mp 25°C): ^{31}P NMR (toluene) +11.6 (s); ^1H NMR (CDCl_3) 1.02 (d, $J(\text{HH}) = 7$ Hz, 6 H, CH_3CNN), 1.05 (d, $J(\text{HH}) = 7$ Hz, 6 H, CH_3CNN), 1.20 (d, $J(\text{HH}) = 7$ Hz, 6 H, CH_3CNP), 1.21 (d, $J(\text{HH}) = 7$ Hz, 6 H, CH_3CNP), 2.35 (br s, 1 H, NH), 3.25 (m, 4 H, CH), 3.55 (d, $J(\text{PH}) = 11$ Hz, 3 H, OCH_3); IR (CHCl_3) 3340 and 3200 (NH); mass spectrum m/e 293 (M^+), 194, 178, 115. Anal. Calcd for $\text{C}_{13}\text{H}_{32}\text{N}_3\text{O}_2\text{P}$: C, 53.21; H, 10.99; N, 14.32. Found: C, 53.35; H, 11.08; N, 14.31.

Photolysis of the Azidobis(diisopropylamino)phosphine Sulfide (3). A solution of **3** (0.25 g, 0.819 mmol) and methanol (0.064 g, 2 mmol) in 6 mL of toluene was irradiated at 254 nm for 18 h at -60°C . The resulting mixture consisted of a mixture of **8** (50%), **9** (45%), and **10** (5%) as shown by ^{31}P NMR. After removal of the solvent at reduced pressure, compounds **8**, **9**, and **10** were isolated by liquid chromatography.

8: R_f 0.46 (ether/petroleum ether 50/50); mp 85°C ; ^{31}P NMR (CDCl_3) +61 (s); ^1H NMR (CDCl_3) 1.25 (d, $J(\text{HH}) = 7$ Hz, 12 H, CH_3), 1.26 (d, $J(\text{HH}) = 7$ Hz, 12 H, CH_3), 2.69 (br s, 2 H, NH), 3.65 (d of sept, $J(\text{HH}) = 7$ Hz, $J(\text{PH}) < 0.3$ Hz, 4 H, CH); IR (CHCl_3) 3480 and 3380 (NH_2) cm^{-1} ; mass spectrum m/e 279 (M^+), 179, 147. Anal. Calcd for $\text{C}_{17}\text{H}_{30}\text{N}_3\text{PS}$: C, 51.58; H, 10.82; N, 15.04. Found: C, 51.72; H, 10.86; N, 15.10.

9: R_f 0.35 (ether/petroleum ether 30/70); mp 32°C ; ^{31}P NMR (CDCl_3) +74 (s); ^1H NMR (CDCl_3) 1.05 (d, $J(\text{HH}) = 7$ Hz, 12 H, CH_3CNN), 1.22 (d, $J(\text{HH}) = 7$ Hz, 6 H, CH_3CNP), 1.24 (d, $J(\text{HH}) = 7$ Hz, 6 H, CH_3CNP), 3.40 (m, 4 H, CH), 3.72 (d, $J(\text{PH}) = 14$ Hz, 3 H, $\text{CH}_3\text{O-P}$); IR (CCl_4) 3320, 3275 (NH) cm^{-1} ; mass spectrum m/e 308 (M^+), 209, 194, 163, 115, 110. Anal. Calcd for $\text{C}_{13}\text{H}_{32}\text{N}_3\text{OPS}$: C, 50.45; H, 10.42; N, 13.58. Found: C, 50.32; H, 10.48; N, 13.70.

10: R_f 0.7 (MeOH/petroleum ether 5.95); mp 147°C ; ^{31}P NMR (CDCl_3) +18 (s); ^1H NMR (CDCl_3) 1.18 (d, $J(\text{HH}) = 7$ Hz, 12 H, CH_3), 1.22 (d, $J_{\text{HH}} = 7$ Hz, 12 H, CH_3), 2.53 (br s, 2 H, NH); 3.4 (d of sept, $J(\text{HH}) = 7$ Hz, $J(\text{PH}) < 0.3$ Hz, 4 H, CH); IR (KBr) 3270 (NH), 1210 (P=O) cm^{-1} ; mass spectrum m/e 263 (M^+) 163. Anal. Calcd for $\text{C}_{12}\text{H}_{30}\text{N}_3\text{OP}$: C, 54.72; H, 11.48; N, 15.96. Found: C, 54.60; H, 11.56; N, 16.01.

Photolysis of the Phenyliminobis(diisopropylamino)phosphine Azide (4). Irradiation of a solution of **4** (0.273 g, 0.75 mmol) in hexane (6 mL) at 254 nm for 24 h at room temperature produced black crystals which precipitated from the solution. After several rinses with hexane and sublimation ($100\text{--}110^{\circ}\text{C}$ (10^{-2} mmHg)) 0.048 g (19% yield) of **13** was obtained, mp 145°C ; ^{31}P NMR (CDCl_3) 51.04 (s); ^1H NMR (CDCl_3) 1.20 (d, $J(\text{HH}) = 7$ Hz, 24 H, CH_3), 3.55 (sept, $J(\text{HH}) = 7$ Hz, 4 H, CH), 6.5–6.9 [m, 4 H, H (arom)]; IR (CH_3CN) 3462 (NH), 1246 (P=N) cm^{-1} ; mass spectrum m/e 336 (M^+), 283, 236. Anal. Calcd for $\text{C}_{18}\text{H}_{33}\text{N}_4\text{P}$: C, 64.25; H, 9.89; N, 16.65. Found: C, 64.42; H, 9.88; N, 16.74.

Photolysis of the Phosphine Azide 1 in the Presence of Trapping Agent. In a typical experiment the phosphine azide **1** (150 mg, 0.549 mmol) in 0.5 mL of deuterated benzene was irradiated at 300 nm at room temperature for 6 h in the presence of an equimolecular amount of trapping agent, methanol, dimethylamine, chlorotrimethylsilane, water, phenyl isocyanate, or azidotrimethylsilane. The structures of the air-sensitive products were determined in deuterated benzene solution.

14: ^{31}P NMR (C_6D_6) +34 (s); ^1H NMR (C_6D_6) 1.2 (d, $J(\text{HH}) = 7$ Hz, 12 H, CH_3C), 1.3 (d, $J(\text{HH}) = 7$ Hz, 12 H, CH_3C), 3.4 (sept-like, 4 H, CH-), 3.5 (d, $J(\text{PH}) = 12$ Hz, 3 H, CH_3O); IR (C_6D_6) 1210

(P=N) cm^{-1} ; mass spectrum m/e 277 (M^+).

17: ^{31}P NMR (C_6D_6) +32.3 (s); ^1H NMR (C_6D_6) 1.21 (d, $J(\text{HH}) = 6.25$ Hz, 12 H, $\text{CH}_3\text{-C}$), 1.32 (d, $J(\text{HH}) = 6.25$ Hz, 12 H, $\text{CH}_3\text{-C}$), 2.6 (d, $J(\text{PH}) = 9.5$ Hz, 6 H, $\text{CH}_3\text{-N}$), 3.46 (sept-like 4 H, CH-); IR (C_6D_6) 1306 (P=N) cm^{-1} ; mass spectrum m/e 290 (M^+).

18: mp 80°C (0.01 mmHg); ^{31}P NMR (C_6D_6) -7.9 (s); ^1H NMR (C_6D_6) 0.27 (s, 9 H, CH_3Si), 1.2 (d, $J(\text{HH}) = 7$ Hz, 12 H, $\text{CH}_3\text{-C}$), 1.3 (d, $J(\text{HH}) = 7$ Hz, 12 H, $\text{CH}_3\text{-C}$), 3.5 (sept-like, 4 H, CH-); IR (C_6D_6) 1260 (P=N) cm^{-1} ; mass spectrum m/e 355 (M^+). Anal. Calcd for $\text{C}_{15}\text{H}_{37}\text{N}_3\text{ClPS}$: C, 50.89; H, 10.54; N, 11.87. Found: C, 50.78; H, 10.60; N, 11.96.

20: ^{31}P NMR (C_6D_6) +6.4 (s); ^1H NMR (C_6D_6) 1.17 (d, $J(\text{HH}) = 7$ Hz, 12 H, CH_3C), 1.20 (d, $J(\text{HH}) = 7$ Hz, 12 H, CH_3C), 3.3 (sept-like, 4 H, CH-), 7.05 (m, 5 H, H arom); ^{13}C NMR [^1H] (C_6D_6) 22.30 and 22.70 (s, CH_3C), 45.99 and 46.03 (s, CH-), 124.75, 125.45, 129.72, and 137.64 (s, C arom), 131.27 (s, N=C=O); IR (C_6D_6) 2165 (N=C=O), 1315 (P=N) cm^{-1} ; mass spectrum m/e 364 (M^+).

21: ^{31}P NMR (C_6D_6) -9.3 (s); ^1H NMR (C_6D_6) 0.2 (s, 9 H, CH_3Si), 1.2 (d, $J(\text{HH}) = 7$ Hz, 12 H, CH_3C), 1.29 (d, $J(\text{HH}) = 7$ Hz, 12 H, CH_3C), 3.4 (sept-like, 4 H, CH-); IR (C_6D_6) 2160 (N_3), 1290 (P=N) cm^{-1} ; mass spectrum m/e 360 (M^+).

Photolysis of the Phosphine Azide 1 in the Absence of Any Trapping Agent. A solution of the phosphine azide **1** (1 g, 3.6 mmol) in 20 mL of benzene was irradiated at 300 nm at room temperature for 18 h. After evaporation of the solvent under reduced pressure, the residue was recrystallized from a mixture of chloroform and acetonitrile (80/20). Repeated recrystallizations afforded 0.74 g of **32** (42% yield) as white crystals. **33** was obtained after purification of the residue by liquid chromatography (R_f 0.6; ether/petroleum ether, 30/70) as white crystals (0.07 g, 3% yield).

32: mp 110°C ; ^{31}P NMR (C_6D_6) +41.11; ^1H NMR (C_6D_6) 1.47 (d, $J(\text{HH}) = 6.82$ Hz, 48 H, $\text{CH}_3\text{-C}$), 4.37 (sept-like, $J(\text{HH}) = 6.82$ Hz, 8 H, CH-); ^{13}C NMR [^1H] (C_6D_6) 24.57 (s, CH_3C), 47.39 (br s, CH-); IR (KBr) 1200 (P=N), 900 (P-N) cm^{-1} ; mass spectrum m/e 490 (M^+), 390 [$\text{M-N}(i\text{-Pr})_2$], 290 [$\text{M-2N}(i\text{-Pr})_2$], 190 [$\text{M-3N}(i\text{-Pr})_2$]. Anal. Calcd for $\text{C}_{24}\text{H}_{56}\text{N}_6\text{P}_2$: C, 58.74; H, 11.50; N, 17.13. Found: C, 58.75; H, 11.50; N, 17.15.

33: mp 125°C ; ^{31}P NMR [^1H] (CDCl_3) +21.44 (d, $J(\text{PP}) = 38$ Hz, $>\text{P=}$), -4.17 (t, $J(\text{PP}) = 38$ Hz, $=\text{P-H}$); ^1H NMR (CDCl_3) 1.34 (d, $J(\text{HH}) = 7.2$ Hz, 12 H, $\text{CH}_3\text{-NPH}$), 1.42 (d, $J(\text{HH}) = 7.6$ Hz, 24 H, $\text{CH}_3\text{-NPN}$), 1.45 (d, $J(\text{HH}) = 7.6$ Hz, 24 H, $\text{CH}_3\text{-NPN}$), 3.9 (sept-like, 10 H, CH-), 7.4 (d of t, $J_{\text{PH}} = 520$, 3 Hz, 1 H, P-H); ^{13}C NMR [^1H] (CDCl_3) 21.4, 21.96, and 22.23 (s, CH_3C), 43.37 (s, CH-); IR (KBr) 2340 (P-H), 1190 (P=N) cm^{-1} ; mass spectrum m/e 636 (M^+), 536 [$\text{M-N}(i\text{-Pr})_2$], 436 [$\text{M-2N}(i\text{-Pr})_2$], 336 [$\text{M-3N}(i\text{-Pr})_2$]. Anal. Calcd for $\text{C}_{30}\text{H}_{71}\text{N}_8\text{P}_3$: C, 56.57; H, 11.23; N, 17.60. Found: C, 56.53; H, 11.22; N, 17.61.

Acknowledgment. Thanks are due to G. Trinquier for helpful discussions, M. Koenig for the ozonolysis reaction, A. Jacquey for technical assistance, and the CNRS (ATP Concepts Nouveaux de l'Objectif Chimie Fine) for financial support.

Registry No. 1, 56183-64-3; **2,** 96455-31-1; **3,** 96455-32-2; **4,** 96455-33-3; **5,** 96481-43-5; **6,** 96455-34-4; **8,** 96455-35-5; **9,** 96455-36-6; **10,** 90670-66-9; **13,** 96455-37-7; **14,** 90670-63-6; **17,** 90670-64-7; **18,** 90670-65-8; **20,** 90670-67-0; **21,** 96455-38-8; **23,** 96455-40-2; **32,** 91842-13-6; **33,** 96455-39-9; Me_3SiN_3 , 4648-54-8; $[(i\text{-Pr})_2\text{N}]_2\text{PCL}$, 56183-63-2; PhN_3 , 622-37-7.