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Selective Preparation of Phosphorus Mononitride (P≡N) from Phosphinoazide and Reversible Oxidation to Phosphinonitrene

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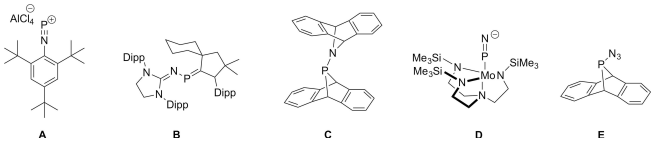
Abstract: The interstellar candidate phosphorus mononitride PN, a metastable species, was generated through high-vacuum flash pyrolysis of (*o*-phenyldioxyl)phosphinoazide in cryogenic matrices. Although the PN stretching band was not directly detected because of its low infrared intensity and possible overlaps with other strong bands, *o*-benzoquinone, carbon monoxide, and cyclopentadienone as additional fragmentation products were clearly identified. Moreover, an elusive *o*-benzoquinone-PN complex formed when (*o*-phenyldioxyl)phosphinoazide was exposed to UV irradiation at $\lambda = 254$ nm. Its recombination to (*o*-phenyldioxyl)-λ^5-phosphinonitrile was observed upon irradiation with the light at $\lambda = 523$ nm, which demonstrates for the first time the reactivity of PN towards an organic molecule. Energy profile computations at the B3LYP/def2-TZVP density functional theory level reveal a concerted mechanism. To provide further evidence, UV/Vis spectra of the precursor and the irradiation products were recorded and agree well with time-dependent DFT computations.

Introduction

Phosphorus mononitride PN, the simplest molecule containing phosphorus and nitrogen that both are essential elements of life, is the phosphorus-bearing interstellar species that is not only the first to be detected but also the one with the highest number of detections in star-forming regions.[1–6] It was first generated in the laboratory by microwave discharging of a P_4/N_2/Ar mixture; an alternative precursor is P_3N_5.[7] Gas-phase thermolysis of dimethyl phosphoramidate (DMPR) revealed that PN is the most prevalent species in its decomposition.[8] Because of its thermodynamically unstable nature, the spontaneous trimerization into cyclotriphosphazene (P_3N_3) was observed even in Kr-matrix at 30 K,[7] which makes studies of the reactivity of "free" PN scarce. Despite numerous experimental and theoretical reports on the interaction of PN with metal atoms (e.g., Cu, Ag, Au, Co, Ni, and Pd),[9,10] its reactivity with organic compounds remains unknown. In contrast to N_2 and P_2, PN does not form a stable coordination complex with vanadium.[11–13] Molecular systems that can serve as "clean PN" precursors are scarce.

Pioneering work by Niecke and co-workers described the first synthesis of a stable compound with a PN triple bond (**A**) (Scheme 1).[14] Bertrand and co-workers reported the synthesis of a stable formal carbene adduct of phosphorus mononitride NHC=N–P=CAAC (**B**; NHC = (NHC(Dipp))$_2$C, Dip = 2,6-(diisopropyl)phenyl, CAAC = cyclic alkyl amino carbene).[15] They also described the one-electron oxidation of PN to the isolable PN radical cation.[15] Velian and Cummins reported an elegant approach to generate PN in solution using anthracene (An = $C_{14}H_{10}$) based precursor (**C**) by extrusion of two molecules of $C_{14}H_{10}$ for the release of PN in solution.[16] However, they only observed anthracene and insoluble material. In 2014, Schulz et al. reported the synthesis of reactive P=N-bearing species by elimination of two molecules of TMS-Cl from (TMS)$_2$NPCl$_2$.[17] Product analysis of the trapping experiments with dimethylbutadiene (dmb) indicates that $Me_3SiN{=}PCl$ formed as a highly reactive intermediate, which eventually oligomerized to cyclo-tetraphosphazene ([PN-(dmb)]$_4$. The first bimetallic complex featuring a P=N bridge, [Fe]-N=P-[Mo], within which the iron could be disengaged by *tert*-butyl isocyanide to form the terminal PN coordination complex [Mo](PN)$^-$ (**D**).[10] The photoinduced isomerization from kinetically stable [Mo](PN)$^-$ to N-bond isomer [Mo](NP)$^-$ was also detected.[10] Very recently, Cummins and co-workers leaped forward when they reported the release of PN via thermolysis of highly explosive AnPN$_3$ (**E**) and trapping PN with [(dppe)Fe(Cp*)-(NP))][BArF$_{24}$], which revealed the reactivity of PN towards transition metal complexes in solution.[18] To our knowledge, this remains the only example of a direct capture of PN.



Scheme 1. Previously reported molecules featuring PN moieties.

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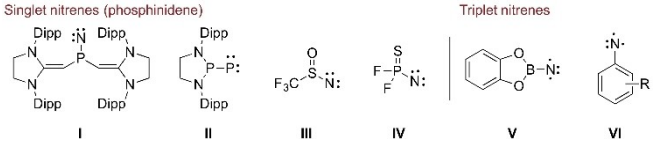
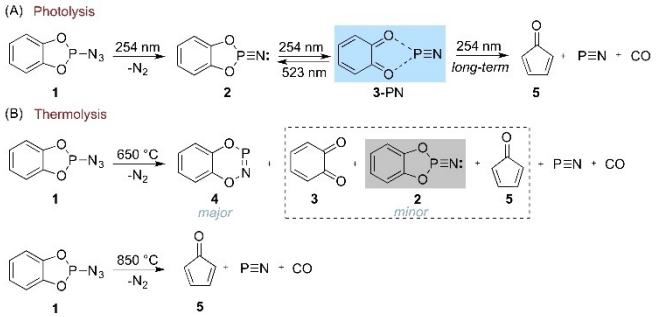
Moreover, in 2009, Cummins and co-workers presented another interesting molecule that possesses a hidden AsP moiety in AsPNMes* ligand complexed with tungsten pentacarbonyl $W(CO)_5$, which was shown to be susceptible to the loss of the $(AsP)W(CO)_5$ unit upon thermolysis. Even though it is bound by $W(CO)_5$, the AsP motif retains its triple bond reactivity with organic dienes.[19]

The thermally and photochemically induced elimination of nitrogen (N_2) from suitable azide precursors has proven to be a reliable method for the synthesis of reactive species.[20–22] It was demonstrated recently that phosphonic azides can be readily triggered thermally and photochemically to release N_2 and leave behind highly reactive species.[23] Bertrand and colleagues reported the synthesis of bis(imidazolidin-2-iminato)phosphinonitrene (**I**) from the corresponding azide upon irradiation at 254 nm, which is stable for days at room temperature[24] and adopts a singlet electronic ground state due to the interaction of the phosphorus lone pair with a vacant orbital of the nitrene.[25] Singlet phosphinophosphinide (**II**) was isolated in an analogous fashion.[26] The existence of singlet nitrenes, such as sulfinylnitrene (**III**) and thiophosphorylnitrene (**IV**), was confirmed by matrix isolation spectroscopy (Scheme 2).[27,28] In contrast to **I**, donor atom stabilized borylnitrene, 2-nitreno-1,3,2-benzodioxaborole (**V**) displays a triplet electronic ground state, which was confirmed by matrix isolation IR, UV/Vis, and EPR spectroscopy and by monitoring its reactivity with dinitrogen, molecular oxygen, carbon monoxide, and carbon dioxide.[29,30] In general, aryl and alkyl substituted nitrenes have triplet electronic ground states, making them highly transient species, and their detection usually requires time-resolved spectroscopy or cryogenic temperatures (**VI**).[31]

It should be stressed that there is no report on the structure and reactivity of PN with organic molecules so far. Experimentally monitoring such species is challenging because the intermediates are often elusive. Here, we report the generation of a weakly bound complex of PN with *o*-benzoquinone (**3**) by UV irradiation of (*o*-phenyldioxyl)phosphinoazide (**1**) in argon matrices, which is stabilized by O···P interactions in **3**-PN. This complex is highly photolabile and converts to (*o*-phenyldioxyl)-λ^5-phosphinonitrene (**2**) upon irradiation with light at $\lambda =$ 523 nm. Photoreversion can be further achieved upon UV light ($\lambda = 254$ nm) irradiation (Scheme 3A). In contrast to the observations in the photolysis experiments, pyrolysis of **1** at 650 °C leads to the formation of 1,4,3,2-benzodioxaphosphorine (**4**) as the major product. Pyrolysis of **1** at 850 °C yields PN, cyclopentadienone (**5**), and carbon monoxide (Scheme 3B). To the best of our knowledge, this is the first spectroscopic example of a PN bearing organic complex that displays reversible covalent bond formation.



Scheme 2. Experimentally known singlet and triplet nitrenes.



Scheme 3. Photochemical and thermal generation of **2** and **3** from **1** and subsequent reactivity.

Results and Discussion

Our initial idea was to generate **2** by photolysis or/and pyrolysis of the corresponding azide precursor **1** followed by immediate matrix isolation at 10 K in solid argon, which would then allow us to investigate the reactions of **2** with small molecules. To generate **2**, azide **1** was isolated at 10 K in an argon matrix, which shows excellent agreement between the experimental and computed IR spectrum. Photolysis of **1** with light at $\lambda = 254$ nm for several minutes resulted in the complete bleaching of the IR bands of **1** and a set of new IR absorptions was detected (Figure 1). Short-wavelength irradiation resulted in the continuous growth of the signals of **2** (Figure S1). However, the photolysis experi-

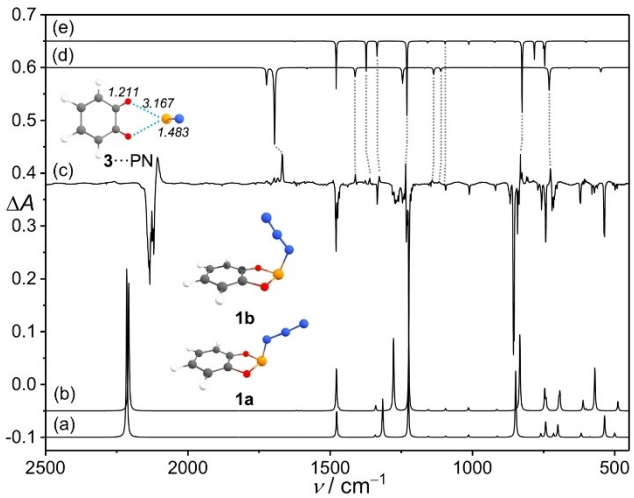


Figure 1. a) Scaled computed infrared (IR) spectrum of **1a** (factor 0.98). b) Scaled computed IR spectrum of **1b** (factor 0.98). c) IR difference spectrum shows the changes upon 6 min 254 nm. d) Scaled computed IR spectrum of **3**-PN (factor 0.98). e) Scaled computed IR spectrum of **2** (factor 0.98). The computed molecular structures for **1a**, **1b**, and 3-PN and bond lengths (in italics, Å) for **3**-PN are also depicted. All computations were done at the B3LYP/def2-TZVP level of theory.

ment revealed another set of rather intense new signals at 1669 (with satellites), 1412, 1276, and 726 cm^{-1}, which show identical growth behavior upon photolysis. The strong band at 1669 cm^{-1} suggests the presence of a carbonyl group within the conjugated system. Hence, by scrutinizing the structure of the precursor, **3** is the most likely candidate.[32] For example, the C=O stretching vibration of 1,4-benzoquinone (*p*-benzoquinone) was reported at 1671 cm^{-1} in argon matrices.[33] The ambiguous identification of **3** is also supported by comparison of the experimentally observed spectrum with the computed spectrum of **3** at the B3LYP/def2-TZVP level of theory (Table S1). Logically, the remaining fragment must be phosphorus nitride PN and it is likely that this new compound is a complex between **3** and PN (**3**-PN) (Table S1). Comparing the frequencies of **3** moiety in the complex with the results of pyrolysis experiments, some small shifts can be observed. Our extensive efforts to identify free PN in an argon matrix have been unsuccessful, due to the low intensity and the apparent overlap with some other bands of **2** and **3**.

To gain more information on the photochemical reactivity of **3**-PN, the mixture was photolyzed at 10 K with light of different wavelengths. Thus, irradiation with $\lambda = 523$ nm resulted in the disappearance of IR bands of **3**-PN and the parallel formation of strong IR absorptions at 1480, 1360, 1327, 1234, 831, 805, and 744 cm^{-1} (Figure 2 and Figure S2). The photolysis product of **3**-PN at this wavelength was identified as **2** (Table S2). With the help of the computations, additional IR bands of medium and weak intensity at 1472, 1011, 1360, 924, and 759 cm^{-1} were assigned to **2** (Table S2). This photoisomerization is reversible and **3**-PN can be regenerated upon irradiation at $\lambda = 254$ nm. The reversible photochemistry (Scheme 3) demonstrates that **2** and **3**-PN exist in equilibrium. This photoinduced reversible process is also observed in the photolysis experiment of (*o*-phenyldioxyl)phosphinoisocyanate (Figure S3). Upon subsequent 523 nm irradiation, regenerated **2** reacts with CO in situ and finally gives (*o*-phenyldioxyl)phosphinoisocyanate.

The formation of **2** and **3**-PN from **1** was also monitored by UV/Vis spectroscopy. In line with the IR experiments, the transitions at 197, 206, 272, and 278 nm of **1** vanish upon irradiation ($\lambda = 254$ nm), and simultaneously the formation of transitions at 268 nm (moderate) and 378 nm (weak, broad) (Figure 3, dashed line) appear. All bands of **3**-PN correlate well with the values of the electronic excitations at 229, 248 nm (f = 0.052 and 0.053), and 352, 378, and 408 nm (f = 0.012, 0.04, and 0.034) computed at TD–B3LYP/def2-TZVP. The broad band at 378 nm corresponds a $\pi \rightarrow \pi^*$ transition. Subsequent irradiation of the sample with $\lambda =$ 523 nm led to the disappearance of UV/Vis bands of **3**-PN and the concomitant appearance of the UV/Vis bands of **2** (Figure S4).

In order to prepare **2** and **3**, we also carried out vacuum flash pyrolysis (VFP) of **1** at 650, 700, and 850 °C (Figure S5). Sander and co-workers reported that triplet phenyl nitrene can be generated in good yields by thermolysis of phenylazide and that it can be subsequently isolated in inert gas matrices.[34] Pyrolysis of **1** at 450 °C results in almost no decomposition of **1**, and only a small amount of **2** and **3** were identified. At 650 °C, the pyrolysis products show new IR bands that were not present in the photochemical route. The infrared spectrum of VFP products of **1** shows several new strong absorptions at 1500, 1240, 1220, 800, and 750 cm^{-1} that we assigned to structure **4**. For example, the strong IR bands at 1500 and 1240 cm^{-1} are attributed to the C=C stretching and CH out-of-plane bending modes of **4** (Table S3). The experimental and computed IR spectra are in good agreement, thereby supporting the assignment of the postulated structure **4**. Note that a small amount of **2** and **3** was observed in the experimental IR spectrum. When the temperature is raised to 850 °C, **5** and CO can be found as main products in the spectrum (Figure S5). This kind of

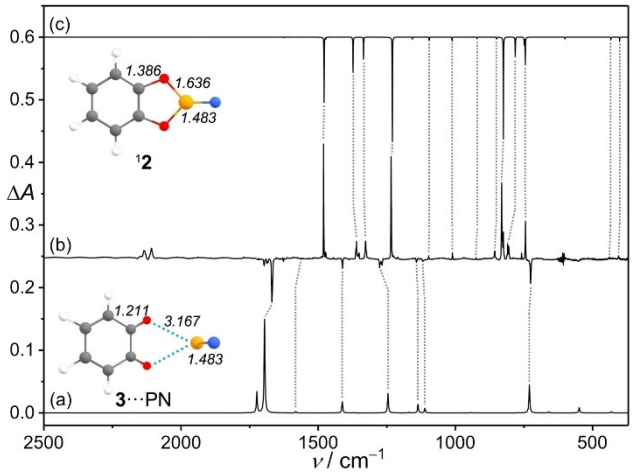


Figure 2. a) Scaled computed IR spectrum for **3**-PN (factor 0.98). b) IR difference spectrum shows the changes upon subsequently 8 min 523 nm irradiation after 254 nm UV irradiation. c) Scaled computed IR spectrum for **2** (factor 0.98). The computed molecular structures and bond lengths (in italics, Å) for **2** and **3**-PN are also depicted. All computations were done at the B3LYP/def2-TZVP level of theory.

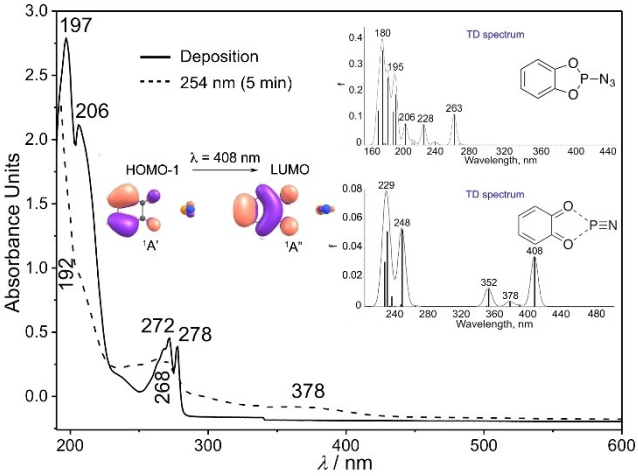


Figure 3. Solid line: UV/Vis spectrum of **1** isolated in argon at 10 K. Dashed line: UV/Vis spectrum of **3**-PN at 10 K: the photochemistry of **1** after irradiation at $\lambda = 254$ nm in argon at 10 K. Inset: Computed [TD-B3LYP/def2-TZVP] electronic transitions for **1** and **3**-PN.

decomposition was also found in the pyrolysis of *o*-phenylene sulfite with loss of sulfonic monoxide as monitored by mass spectrometry, which further lends credibility to our identification.[35]

When the pyrolysis experiment was carried out at 850 °C, only a small amount of **4** formed. Instead, the intense absorption bands at 1735, 1333, 952, 843, and 651 cm^{-1} provide evidence for the formation of cyclopentadienone (**5**) as the major product. The absorption bands of **6** are in agreement with the previously reported IR values of **5** in neon matrix.[36] Pyrolysis of **1** at 850 °C produces a large amount of carbon monoxide (CO), apparent by the strong absorption band at 2139 cm^{-1}, which most probably derives from the gas-phase decarbonylation of **3**; the latter forms by stepwise elimination of N_2 and PN from **1**. Pyrolysis of **1** at 850 °C is strongly dominated by entropy that preferentially leads to **5** and CO (Figure S5).

To gain insight into the mechanism of these reactions, we computed the relevant parts of the potential energy hypersurface surrounding **1** at B3LYP/def2-TZVP (Figure 4). According to these computations, **1** can exist in *anti* and *syn* conformations (**1a** and **1b**) with orientations of azide group relative to the opposing phenyl group; **1a** is 1.4 kcal mol^{-1} more stable than **1b**, and the rotational barrier connecting the two species amounts to 2.5 kcal mol^{-1} (including zero-point vibrational energy correction, ZPVE). Obviously, the formation of **2** and PN from **1** is a multistep process. The reaction path implies the cleavage of N_2 from **1b** to produce nitrene **2** via **TS2**. The barrier for this process is 31.3 kcal mol^{-1}. The subsequent loss of PN leads to the formation of the **3**-PN complex with a stabilization energy of 2.6 kcal mol^{-1}. The transition structure (**TS3**) for the concerted loss of PN from **2** is associated with a barrier of 38.0 kcal mol^{-1}. Moreover, we performed a two-dimensional relaxed scan along the O1-P and O2-P bonds in **2** using the RI–B3LYP/def2-TZVP method. A saddle point was found on the concerted path, indicating that the decomposition of **2** into **3**-PN is a concerted process (Figure S6 Supporting Information). The pyrolysis of starting material **1** at 700 °C also yielded infrared signals that were identified as **4**. The rearrangement of **2** to **4** is endothermic by +11.1 kcal mol^{-1} with an activation barrier of 47.2 kcal mol^{-1}. A second pathway describes a one-step process for the formation of **4** from **1a** through a barrier (**TS5**) of 47.5 kcal mol^{-1}. The intrinsic reaction paths associated with the rearrangement of **2** to **4** and **1a** to **4** are almost isoenergetic. The pyrolysis temperature at 850 °C promotes further decarbonylation of **3** and gave IR signals that were identified as **5**. The transition structure of this dissociation is associated with a substantial barrier of 61.9 kcal mol^{-1} (**TS7**).

According to our computations, **2** has a large singlet-triplet energy separation of $\Delta E_{ST} = -22.2$ kcal mol^{-1} at B3LYP/def2-TZVP, underlining its singlet ground-state nature. Nitrene **2** displays a C_{2v} point group with a $^1A_1$ electronic ground state, as a result of π-type stabilization of the electron-deficient nitrene center through the adjacent phosphorus *p*-lone pair. The PN bond length in **2** is 1.483 Å, which lies in the range of a P≡N triple bond. For example, the PN bond lengths in Mes-N≡P (**A**) (Mes = 2,4,6-tri-*tert*-butylphenyl) and bis(imidazolidin-2-iminato)phosphinonitrene (I) are 1.475 and 1.456 Å respectively.[14,24] A Wiberg bond index of 3.11 was computed for the PN bond in **2**, confirming the presence of a PN triple bond. Natural bond orbital (NBO) computations indicate that the nitrogen atom possesses a large negative charge (−1.02*e*), whereas phosphorus atom carries a large positive charge (+1.92*e*). The NBO charges at the oxygen atoms in **2** are −0.69, indicating zwitterionic character. This is in line with a natural resonance theory (NRT) analysis, which favors the zwitterionic resonance contributor (Figure S7). Our computational analysis for the **3**-PN complex gave a binding energy of −2.6 kcal mol^{-1} at B3LYP/def2-TZVP and of −6.0 kcal mol^{-1} at B3LYP–D3(BJ)/def2-TZVP. Complex **3**-PN is stabilized by electrostatic interactions between O···P with a shared potential electron density (ρ) of 0.0087 and a second Hessian eigenvalue (λ_2) of −0.0087 as derived from a topological non-covalent interaction (NCI) analysis (Figure 5 and Table S4),[37] which is consistent with the computed properties of the O···P interaction in the HO···PO complex (Figure S8).[38] The O···P distance in **3**-PN of 3.166 Å is smaller than the sum of the van der Waals radii of O (1.52 Å) and P (1.80 Å), respectively.[39]

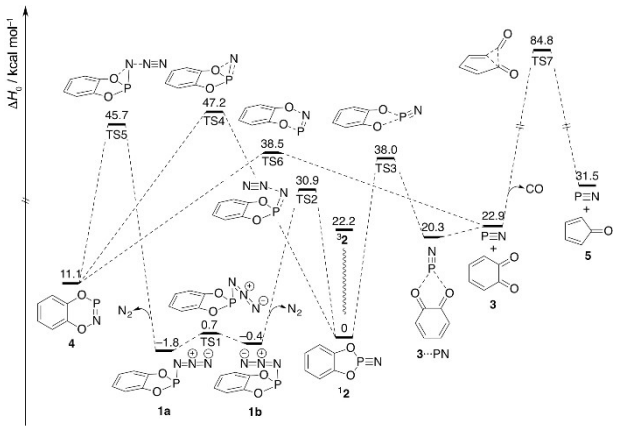


Figure 4. Potential energy hypersurface profile (ΔH_0, kcal mol^{-1}) of the reactions of **2** at B3LYP/def2-TZVP + ZPVE at 0 K.

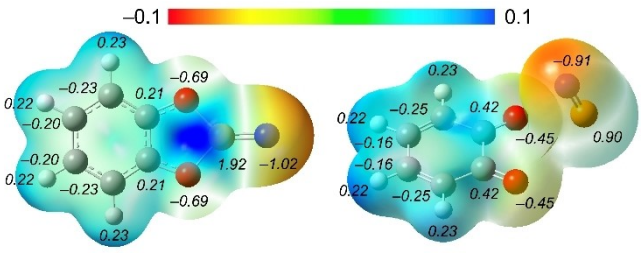


Figure 5. Calculated molecular electrostatic potential (ESP) maps (isovalue = 0.004) and natural population analysis (NPA) charges (numbers in italics) for **2** (left) and **3**-PN (right) at B3LYP/def2-TZVP.

Conclusion

Here, we report a *o*-benzoquinone-PN complex that was generated in cryogenic matrices utilizing UV light irradiation of the corresponding azide precursor. Besides IR and UV spectroscopic characterization, its recombination to covalently bonded (*o*-phenyldioxyl)-λ^5-phosphinonitrile was triggered by subsequent 523 nm irradiation through a concerted mechanism, which reveals the first observed reactivity of PN towards organic molecules. VFP and photolysis experiments suggest that (*o*-phenyldioxyl)phosphinoazide may be a viable precursor for PN in synthesis, and this will be the target of forthcoming work.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Matrix Isolation · Nitrenes · Phosphorus Mononitride · Photochemistry

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