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Preparation and Characterization of Parent Phenylphosphinidene and its Oxidation to Phenyldioxophosphorane, the Elusive Phosphorous Analogue of Nitrobenzene

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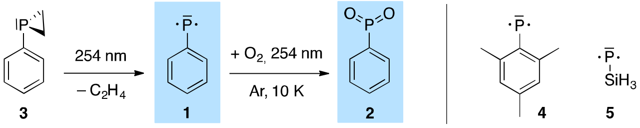
Supporting Information Placeholder

ABSTRACT: Triplet phenylphosphinidene was prepared by light-induced elimination of ethylene from the corresponding phenylphosphirane and was characterized by IR and UV/Vis spectroscopy together with matching of its spectral data with density functional theory (DFT) computations. The photolysis of phenylphosphirane in ^3P-O_2 doped matrices enabled the spectroscopic identification of a hitherto unknown phenyldioxophosphorane, the long elusive phosphorous analogue of nitrobenzene.

Phosphinidenes (R–P̈:) are electron-deficient, neutral, and monovalent phosphorus analogues of carbenes (R–C̈–R′) and nitrenes (R–N̈:). All of these species with R=alkyl, aryl are by definition electron-deficient because their electron octets are incomplete. This makes them typically highly reactive and fleetingly existent, and they have long been considered laboratory curiosities that are, however, highly valuable in extending our level of understanding of chemical bonding and reactivity. While the chemistry of free carbenes and nitrenes has been well established,[1] that of uncomplexed phosphinidenes has just begun blossoming.[2,3] Due to their short life-time and high reactivity, the chemical properties of phosphinidenes have been deduced almost exclusively from trapping or complexation experiments.[4-7] Several methods for the generation of uncomplexed phosphinides have been reported in the literature,[8,9] including attempts towards observation of triplet mesitylposphinidene (**4**) *via* EPR spectroscopy.[10] In 2004 the matrix isolation (in Ar) of silylphosphilide (H_3SiP; **5**) was achieved through the reaction of atomic silicon with PH_3.[11] Phenylphosphinidene **1** is the parent of **4** that has never been observed experimentally. Computational studies predict that **1** has a triplet ground state (referred to as ^{3}**1**), which is 20–25 kcal mol^{-1} lower in energy than the lowest lying singlet state.[12-15] Computational[16] and experimental[17-19] studies suggest that strong π-donor substitution would stabilize the phosphinidene singlet over the triplet state. The chemistry of **4**, in particular, cycloaddition reactions, has been also studied.[20,21] Matrix isolation experiments showed that the photolysis of mesitylphosphirane in solid argon produces **4**, and its IR as well as UV spectra, along with its C–H-bond insertion product 1H,2H-dihydrobenzophosphete could readily be assigned.[22]

As ^{3}**1** is highly reactive, its reactions with small molecules is expected to lead to several interesting novel species that have not been observed. A prime example is the reaction of ^{3}**1** with molecular oxygen (^3P-O_2) that may directly lead to phenyldioxophosphorane ($PhPO_2$, **2**), a novel compound that constitutes the hitherto unknown phosphorous analogue of ordinary nitrobenzene.

Scheme 1. Photochemical generation of 1 and 2.



Such thermal reactions of triplet carbenes and nitrenes with molecular oxygen (^3P-O_2) have been thoroughly studied. Triplet carbenes readily react with ^3P-O_2 to form highly labile carbonyl *O*-oxides that further rearrange to dioxiranes and esters;[23-25] reactions of triplet nitrenes with ^3P-O_2 are much slower.[22,26] The oxidations of arylnitrenes in oxygen-doped argon matrices yields nitroarenes (*vide infra*).[27]

The existence of dioxophosphoranes (RPO_2) to date has only been inferred from trapping experiments.[28-32] Dioxophosphoranes are extremely electrophilic at phosphorous, and show high reactivity when transiently generated in solution; RPO_2 species instantly undergo self-aggregation to form cyclic or linear polymeric compounds.[28,33] For example, the combustion of dimethyl methylphosphonate generates CH_3PO_2 whose molecular mass was detected using mass spectrometry.[34] Chlorodioxosophosphorane ($ClPO_2$) was IR-spectroscopically characterized in an argon matrix *via* the photochemical reaction of ozone with POCl.[35] The argon matrix-isolated IR spectrum of $NaOPO_2$ has also been recorded.[36] However, to the best of our knowledge, there are no reports on the identification and characterization of an uncomplexed metastable phenyldioxophosphorane. Herein, we report the first synthesis, IR, and UV-Vis spectroscopic characterization of phenylphosphinidene (**1**) and its oxidation product phenyldioxophosphorane (**2**). As we will demonstrate, matrix isolation studies of ^{3}**1** reveal unusually high reactivity towards ^3P-O_2, in marked contrast to its nitrene analogue, even at temperatures as low as 10 K.

Following the route for the synthesis of ^{3}**4**,[10,22] we synthesized ^{3}**1** from the phosphirane **3**[37] by UV- irradiation. The photolysis (λ=254 nm) of matrix-isolated **3** in solid argon at 10 K results in the complete disappearance of its IR bands, and a set of new IR absorptions was detected (Fig. 1).

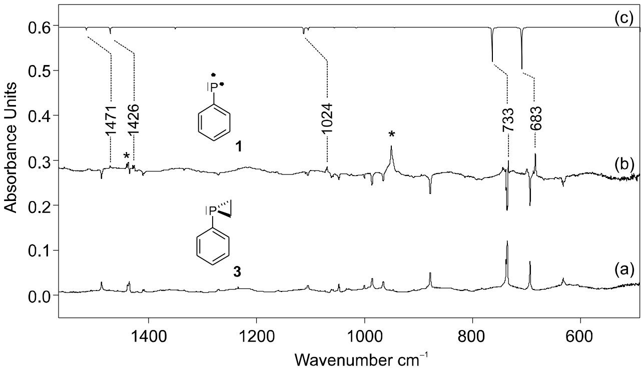


Figure 1. (a) IR spectrum of matrix-isolated **3** in Ar at 10 K. (b) IR difference spectra showing the photochemistry of **3** after irradiation at λ=254 nm in argon at 10 K. Downward bands assigned to **3** disappear while upward bands assigned to ^{3}**1** appear after 15 min irradiation time. (c) IR spectrum of ^{3}**1** computed at M06-2X/6-311++G(2d,2p) (unscaled). Bands attributed to ethylene are marked with an asterisk (*).

The most intense bands are located at 733 and 683 cm^{-1}, which show identical growth behavior upon photolysis. The excellent agreement between the experimental and unscaled M06-2X/6-311++G(2d,2p) as well as B3LYP/cc-pVTZ computed IR spectra is taken as evidence for ^{3}**1** (Fig. 1 and Fig. S1). With the computations additional IR bands of medium intensity at 1556, 1471, 1426, 1069, 1055, 1024, and 994 cm^{-1} were assigned to ^{3}**1** (Fig. 1, and Table S1). Another set of absorption bands located at 1441 and 949 cm^{-1} provide evidence for the presence of ethylene formed as a co-product of the photochemical decomposition of **3** (Fig. 1b).

The UV/Vis spectral analysis of the 254 nm photolysis of **3** shows that its absorption maximum at 230 nm gradually decreases while new absorptions appear. The UV/Vis spectrum of matrix isolated ^{3}**1** reveals a strong absorption band at λ_{max}=264 nm, and two weak absorption bands at λ_{max}=285 and 344 nm, respectively (Fig. 2). It closely resembles the previously reported spectrum of **4** in argon matrix (278, 292, 350, and 420–470 nm) and is in good agreement with its computed UV/Vis spectrum using time-dependent DFT (TD-DFT). TD-M06-2X/6-311++G(2d,2p) computations exhibit two strong transitions at 259 nm (f=0.109) and 265 nm (f=0.179) as well as weak transitions at 333 nm (f=0.0138) and 341 nm (f=0.009).

Unfortunately, all our attempts to record an EPR spectrum of ^{3}**1** failed as the X-band in the range of 0–12000 Gauss was not visible. This is in line with the findings of Bucher et al. where even the W-band only provided a very weak signal.[22]

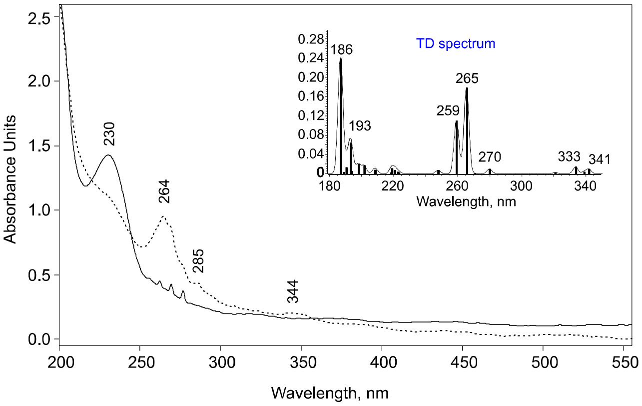
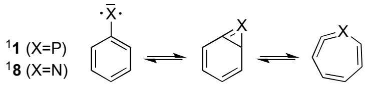


Figure 2. Solid: UV/Vis spectrum of **3** isolated at 10 K in Ar. Dashed: UV/Vis spectrum of ^{3}**1** at 10 K; the photochemistry of **3** after irradiation at λ=254 nm in Ar at 10 K. Inset: Computed [TD-M06-2X/6-311++G(2d,2p)] spectrum of ^{3}**1**.

When the sample was irradiated at λ=312 nm, the IR bands associated with ^{3}**1** and ethylene vanished, whereas the IR bands of the starting material **3** appeared; photolysis at 20 K increased the yield of **2** to ~95%. The reaction of **4** with alkenes upon irradiation in cryogenic matrixes was observed previously by Bucher *et al.*.[22] For **4**, however, this is only a minor reaction with the major product of the photolysis being 1H,2H-dihydrobenzophosphete resulting from intramolecular C–H-bond insertion.

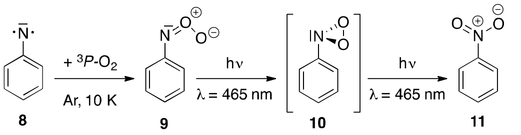
The matrix containing ^{3}**1** was subsequently photoirradiated but ring enlargement products, which are typical for singlet arylnitrenes such as ^{1}**8** (Scheme 2),[38,39] were *not* observed. This is in line with the predictions of Borden and co-workers[12] who have shown with multiconfigurational second-order perturbation theory [(CASPT2/6-31G(d)] that the ring expansion of singlet ^{1}**1** to 1-phospha-1,2,4,6-cycloheptatetraene is an endothermic process, whereas the analogous ring expansion of ^{1}**8** to 1-aza-1,2,4,6-cycloheptatetraene is computed to be exothermic.

Scheme 2. Isomers of singlet phenylphosphinidene ^{1}1 and singlet phenylnitrene ^{1}8.



Recently, Sander *et al.* showed that the thermal reaction of ^{3}**8** with ^3P-O_2 in solid xenon matrices at 40 K gives phenylnitroso oxide **9** (Scheme 3), which rearranges to nitrobenzene upon selective irradiation.[26,40] In line with the reactions of triplet arylcarbenes[23,25] and arylnitrenes,[26,40] ^{3}**1** should react with ^3P-O_2 (Scheme 1). Irradiation (λ=254 nm) of **3** in an argon matrix doped with 3% (i.e., large excess) ^3P-O_2 at 10 K resulted in the almost complete bleaching of the IR bands of **3** and formation of a new compound with strong IR absorptions at 1446, 1416, 1170, 748, 687, and 500 cm^{-1} (Fig. 3a). The major constituent of the photolysis products of starting material **3** was identified as phenyldioxophosphorane **2**. The intense absorption at 500 cm^{-1} (calc.: 512 cm^{-1}) shows an isotopic shift of –12 cm^{-1} (calc.: –12 cm^{-1}) in $^{18}O_2$-**2** and is assigned to the OPO deformation vibration. Two other strong absorptions at 1416 and 1170 cm^{-1} with ^{18}O-isotopic shifts of –39 and –24 cm^{-1} (calc.: –40 and –21 cm^{-1}, respectively) are assigned to the OPO asymmetric and symmetric stretching vibration of **2**, respectively (Fig. 3 and Table S2). The observed vibrational bands match well with the fundamentals of **2** (Table S2) computed anharmonically at M06-2X/6-311++G(2d,2p).

Scheme 3. Reaction of triplet phenylnitrene (8) with ^3P-O_2.



Irradiation of **3** at λ=254 nm in the presence of 0.1–0.5% ^3P-O_2 provided ^{3}**1** as the major product because statistically all reactants are isolated in individual matrix sites. As long as the matrix is kept at 10 K where diffusion does not occur, no reaction is observed. Subsequent annealing (and re-cooling before measurement) of the matrix to 35 K results in diffusion of ^3P-O_2 that produces another set of weak peaks characterized by absorptions at 1110, 744, 690, and 445 cm^{-1} (Fig. S1, Table S3) assigned to 3-phenyl-1,2,3-dioxaphosphirane **7**. Finally, 465 nm irradiation of **7** increases the bands of **2** and leads to the disappearance of the signals of **7** (Fig. S1).

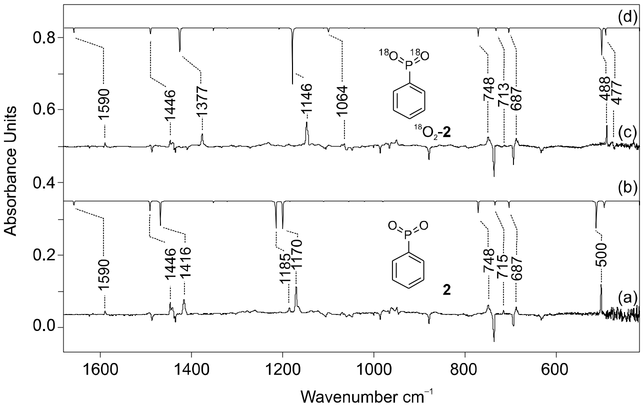


Figure 3. (a) IR difference spectra showing the photochemistry of **3** in the presence of 3% O_2 after irradiation at λ=254 nm in argon at 10 K. Downward bands assigned to **3** disappear while upward bands assigned to **2** appear after 15 min irradiation time. (b) IR spectrum of **2** computed at M06-2X/6-311++G(2d,2p) (unscaled). (c) IR difference spectra showing the photochemistry of **3** in the presence of 3% $^{18}O_2$ after irradiation at λ=254 nm in argon at 10 K. Downward bands assigned to **3** disappear while upward bands assigned to $^{18}O_2$-**2** appear after 15 min irradiation time. (d) IR spectrum of $^{18}O_2$-**2** computed at M06-2X/6-311++G(2d,2p) (unscaled).

By comparison of the IR spectrum with the computed spectra of **6a**, **6b**, and **7**, most of these new peaks correlate well with the IR spectrum computed for **7** (Fig. S1). For confirmation of these assignments, we also performed experiments with ^3P-$^{18}O_2$. In particular, we found a small ^{18}O isotope shift for a band at 1110 cm^{-1} (–2 cm^{-1} expt., –4 cm^{-1} calc.), which was assigned to the C–P stretching vibration of **7**. An experimental ^{18}O isotope shift of –17 cm^{-1} was observed for the CPO deformation vibration, in nice agreement with the computed shift of –17 cm^{-1} (Table S3). The transformation **7** → **2** through transition state TS1 is associated with a barrier of +34.2 kcal mol^{-1} (M06-2X/6-311++G(2d,2p), Fig. S2).

The relative stabilities of the products resulting from oxygenation of ^{3}**1** were computed at M06-2X/6-311++G(2d,2p) + ZPVE (ΔH_0, Fig. 4), which nicely reproduces the experimental IR spectra of ^{3}**1** and **2**; we used this level for the computations of the ground-state properties of **2** and **7**. The reaction of ^{3}**1** with ^3P-O_2 to produce a metastable singlet product is formally spin-forbidden, and the question arises in which step the intersystem crossing occurs along the reaction coordinate. It has been proposed that the photochemical formation of nitro compounds from nitroso oxides proceeds *via* intermediate dioxaziridines (Scheme 3), and the formation of such compounds upon high intensity photolysis of nitroso oxides was observed in glassy matrices.[41] Experimental studies by Bally[26] and Sander[40] indicate the formation of arylnitroso oxides that eventually rearrange to nitroanilines and nitrobenzene by selective irradiation, respectively. No evidence for dioxaziridines as intermediates in the conversion of the nitroso oxides to nitroanilines was found.

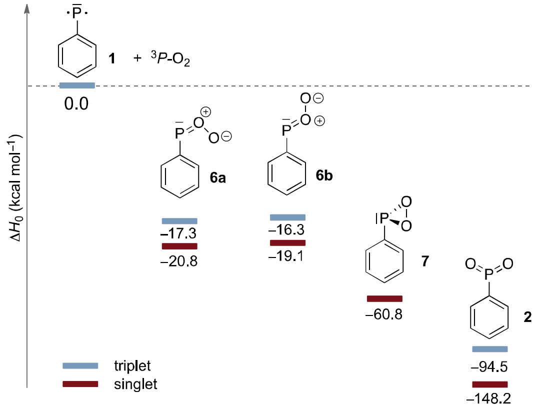
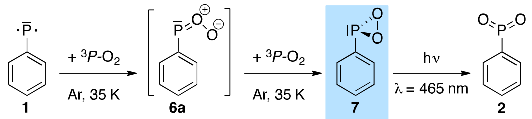


Figure 4. Relative enthalpies (not drawn to scale) of the species involved in the formation of the phenyldioxophosphorane **2** computed at the M06-2X/6-311++G(2d,2p) level of theory.

The thermal reaction of ^{3}**1** with $^3P\text{-}O_2$ at temperatures as low as 40 K is expected to produce triplet diradical / zwitterionic ^{3}**6** as the primary product. Although we were not able to observe **6** spectroscopically, the formation of oxidation products such as **2** or **7**, suggests the intermediacy of these highly labile species. This also implies that the triplet-singlet curve crossing occurs in the structural vicinity of **6** and **7**, an issue that will have to be addressed by sophisticated excited state computations.

Scheme 4. Reaction of triplet phenylphosphinidene 1 with oxygen.



In sum, phenylphosphinidene ^{3}**1** is accessible by matrix photolysis of phenylphosphirane **3**. Under matrix isolation conditions ^{3}**1** is photochemically and thermally stable toward rearrangement to the corresponding 1-phospha-1,2,4,6-cycloheptatetraene in accordance with computational predictions.[12] While ^{3}**1** appears photochemically stable, it reacts quantitatively with $^3P\text{-}O_2$ to give long elusive phenyldioxophosphorane **2**. Moreover, in highly diluted $^3P\text{-}O_2$ doped argon matrixes, ^{3}**1** reacts thermally with oxygen at 35 K to give 3-phenyl-1,2,3-dioxaphosphirane **7**, which is also a new compound. Irradiation at λ=465 nm leads to phenyldioxophosphorane **2** (Scheme 4).

ASSOCIATED CONTENT

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org: IR spectra, IR tables, Cartesian coordinates, absolute energies of all optimized geometries, and experimental procedures (PDF).

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