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Reaction of Triplet Phenylnitrene with Molecular Oxygen

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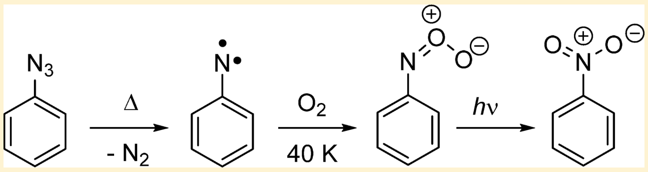
Supporting Information



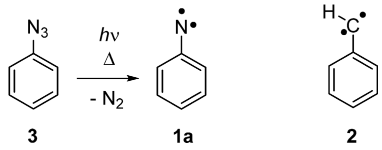
ABSTRACT: Triplet carbenes react with molecular oxygen with rates that approach diffusion control to carbonyl *O*-oxides, whereas triplet nitrenes react much slower. For investigating the reaction of phenylnitrene with O_2, the nitrene was generated by flash vacuum thermolysis (FVT) of phenylazide and subsequently isolated in O_2-doped matrices. FVT of the azide produces the nitrene in high yield and with only minor contaminations of the rearranged products that are frequently observed if the nitrene is produced by photolysis. The phenylnitrene was isolated in solid Ar, Xe, mixtures of these rare gases with O_2, and even in pure solid O_2. At temperatures between 30 and 35 K an extremely slow thermal reaction between the nitrene and O_2 was observed, whereas at higher temperatures, solid Ar and O_2 rapidly evaporate. Only O_2-doped Xe matrices allowed us to anneal at temperatures above 40 K, and at these temperatures, the nitrene reacts with O_2 to produce nitroso *O*-oxide mainly in its *syn* conformation. Upon visible light irradiation (450 nm), the nitroso oxide rapidly rearranges to nitrobenzene.

INTRODUCTION

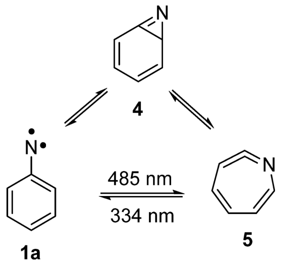
Phenylnitrene **1a** is the prototype of an aromatic triplet ground state nitrene and has therefore been subjected to a large number of experimental and theoretical studies.[1,2] The S-T gap in nitrene **1a** is 18 kcal/mol in favor of the triplet and thus much larger than that of related phenylcarbene **2** (3–4 kcal/mol). The reactivity of nitrene **1a** also differs substantially from that of carbene **2**. Although carbene **2** can be easily trapped in intermolecular reactions, e. g., with molecular oxygen, nitrene **1a** is less reactive and in solution in most experiments forms polymeric tars instead of useful trapping products.[1,3,4] Photolysis of phenylazide **3** in solution in the presence of amines yields azepines and trapping products that could either arise from benzazirine **4** or ketenimine (1-aza-1,2,4,6-cycloheptatetraene) **5**.[5,6]

In early matrix isolation experiments, it was shown that the photolysis of **3** in inert gas matrices produces ketenimine **5** as the main product instead of the expected nitrene **1a**.[7,8] Hayes and Sheridan later demonstrated that **5** is the product of the secondary visible light photolysis of **1a**. If narrow band 334 nm irradiation instead of UV–vis broadband irradiation is used for the photolysis of azide **3** (Scheme 1), phenlynitrene **1a**[9] is formed in 80% yield, and **5** is only a minor product. Nitrene **1a** is highly photolabile, and with 485 nm irradiation, it rapidly rearranges to ketenimine **5** (Scheme 2). Benzazirine **4** could not be spectroscopically detected in these experiments; its formation was only anticipated from trapping experiments.

Scheme 1. Phenylcarbene and Generation of Phenylnitrene from Phenylazide



Scheme 2. Photochemical Interconversion of C_6H_5N Derivatives



An alternative method for producing matrix-isolated phenylnitrene **1a** is the flash vacuum thermolysis (FVT) of **3** with subsequent trapping of the products in solid argon. This method was recently used by Wentrup et al. to study the high temperature thermochemistry of **1a**.[10] One of the main products of the FVT of **3** is cyanocyclopentadiene **10**, and the mechanism of its formation was studied by isotopic labeling.

Because nitrene **1a** has a triplet ground state, it might be expected to react rapidly with molecular oxygen. Triplet carbenes readily react with O_2 to form the highly labile carbonyl *O*-oxides that further rearrange to dioxiranes and esters (Scheme 3).[11−13] Although these reactions have been studied in great detail, the reactions of triplet nitrenes with O_2 have been much less investigated.[14] Sawaki et al. concluded

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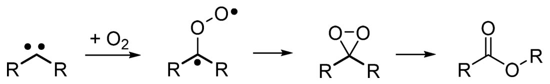
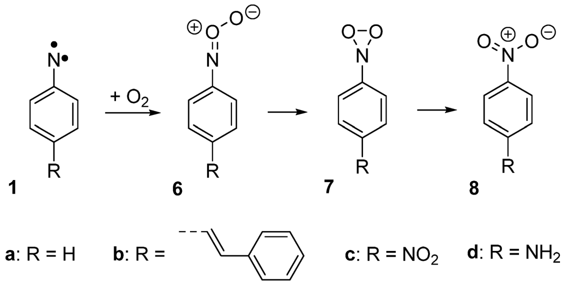
Scheme 3. Reaction of Triplet Carbenes with O_2



from trapping studies that substituted phenylnitrenes react with O_2 to phenylnitroso oxides **6**, which further rearrange to either nitrobenzenes **8** (up to 30% yield) or transfer oxygen atoms to suitable substrates (Scheme 4).[15,16] In O-transfer reactions, nitroso oxides **6** react as electrophilic radicals.[16]

Scheme 4. Reaction of Arylnitrenes 1 with O_2



A basic problem for the spectroscopic characterization of intermediates of the oxygenation of phenylnitrenes **1** is the rapid photochemical rearrangement of the nitrenes to derivatives of **4** and **5**, which leads to unwanted side products. To circumvent these problems, Bendig et al. studied the oxygenation of *p*-nitrenostilbene **1b** and derivatives, which show a lower tendency for rearrangement in methyltetrahydrofuran (MTHF) glasses by UV–vis spectroscopy.[17] Photolysis of azidostilbene in oxygen-containing MTHF at 77 K produces the nitrenostilbene **1b** in high yield, which upon warming to 95 K reacts with O_2 to the nitroso *O*-oxide **6b** with an absorption maximum at 514 nm (Scheme 4). The photochemistry of **7b** proved to depend strongly on the irradiation conditions, and tentative evidence for the formation of the highly labile dioxaziridine **7b** as a precursor of nitrostilbene **8b** as final product was presented.[17]

The first characterization of an aryl nitroso oxide by matrix isolation IR spectroscopy was reported by Inui et al.[18] *p*-Nitrophenylnitrene **1c** was generated by photolysis of *p*-nitrophenylazide matrix-isolated in 5% O_2-doped Xe at 10 K. Nitrene **1c** was selected and not the parent phenylnitrene **1a** because the latter rapidly rearranges to **5** and therefore is obtained only in low yield. If this matrix was warmed to 50 K, the IR bands of **1c** decreased in intensity, and a mixture of the *syn* and *anti* isomers of nitroso oxide **6c** was formed. This assignment was confirmed by ^{18}O isotopic labeling.

In a similar way, the oxygenation of *p*-aminophenylnitrene **1d** was studied by Pritchina, Gritsan, and Bally in 4% O_2-doped argon matrices.[19] Annealing of such matrices for several min at 30 K resulted in a decrease in the IR absorptions assigned to **1d** and the formation of the *syn* and *anti* isomers of nitroso oxide **6d**. By monochromatic irradiation at two different wavelengths, these isomers could be interconverted, whereas broad band irradiation with >365 nm resulted in the rearrangement to *p*-nitroaniline **8d**. These results were corroborated by careful DFT and ab initio calculations. Dioxaziridine **7d** was not observed under any conditions in these experiments. According to the calculations, **7d** is more than 11 kcal/mol higher in energy than **6d**, whereas the rearrangement of **6d** to **8d** releases ~66 kcal/mol. Interestingly, very similar energetics were estimated for the corresponding intermediates in the oxygenation of the parent phenylnitrene **1a**.

For triplet phenylnitrene **1a**, the activation barrier for the reaction with O_2 was determined in flash photolysis experiments to be 4.3 ± 0.5 kcal/mol.[20] Thus, in contrast to the oxygenation of triplet arylcarbenes, there is a considerable activation barrier to overcome. Consequently, the rates for the reactions of **1c** and **1d** with O_2 at room temperature are only 0.8 and 4.5×10^6 M^{-1} s^{-1}, respectively, which are 3 orders of magnitude slower than that of typical arylcarbenes.[21] The reaction of triplet nitrenes with O_2 was studied computationally by Liu, Hadad, and Platz.[22] They concluded that phenylnitrene **1a** reacts much slower with O_2 than phenylcarbene **2** because the former reaction is, with −20.2 kcal/mol (CBS-QB3 calculations), much less exothermic than the latter (−69.9 kcal/mol at the same level of theory). The difference in thermicity results from the weak N–O bond formed in the oxygenation of the nitrene compared to a much stronger C–O bond in the carbene oxygenation reaction. The oxygenation of a borylnitrene was investigated by Bettinger and Bornemann.[23] The primary thermal product is again the corresponding nitroso oxide, which upon photolysis rearranges to a nitritoborane via insertion of one O atom into the BN bond.

To study the reaction of the parent phenylnitrene **1a** with O_2, we generated the nitrene by FVT of phenylazide **3** with subsequent trapping of the products in O_2-doped Ar or Xe matrices. This technique produced clean matrices of **1a** that allowed us to identify the products of the reaction with O_2 by IR spectroscopy.

■ RESULTS AND DISCUSSION

The results of FVT experiments not only depend on the thermolysis temperature but also on the length of the heating zone, the inner diameter of the oven, the wall material, and the pressure inside the oven. FVT experiments are therefore difficult to optimize. In the setup used here (see Experimental Section), phenylazide **3** proved to be rather thermolabile, and at 300 °C, a substantial fraction of **3** was already transformed to nitrene **1a** as the major product.

Nitrene **1a**, trapped in argon at 4 K, was easily identified by its matrix IR spectrum with the strongest absorptions at 747 and 655 cm^{-1}, which nicely match the literature data.[9] The highest yield of **1a** was found at FVT temperatures between 400 and 500 °C, where the IR spectrum of the FVT products is dominated by **1a** (Figure 1). Other IR bands of the FVT products are assigned to remaining precursor **3**, traces of azobenzene **9**, ketenimine **5**, and cyanocyclopentadiene **10** by comparison with the literature data.[7,8,10,24] (Scheme 5). At the lower pyrolysis temperatures, the signals of the precursor are stronger, as expected, whereas at temperatures above 600 °C, nitrile **10** becomes the dominant product in agreement with the literature data.[10,25]

The IR spectra obtained after trapping the products of the FVT of **3** in Xe are very similar to that obtained in Ar (Figure 1b, Table 1). The major differences are broader absorptions and matrix shifts of a few cm^{-1} in solid Xe compared to Ar. Annealing of the matrices at 30 K (Ar) or 50 K (Xe) did not result in major changes of the spectra. These experiments demonstrate that the FVT of phenylazide **3** provides a very clean source of phenylnitrene **1a**.

To investigate the reaction of **1a** with O_2, argon and xenon matrices were doped with 4% of O_2. After deposition at 4 K,

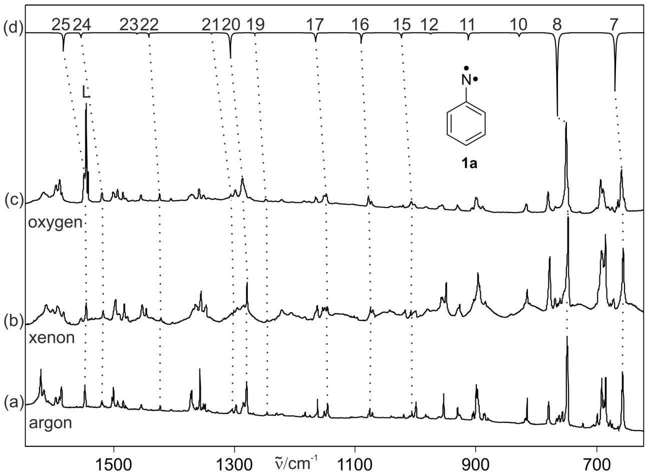
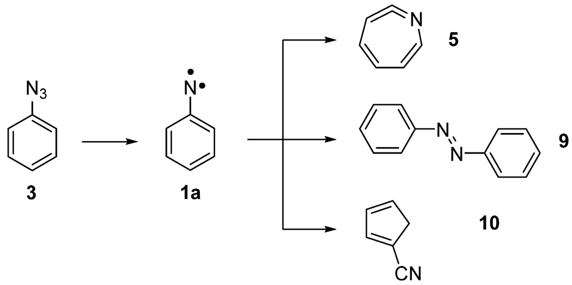


Figure 1. IR spectra showing the products of the FVT of phenylnitrene **1a** at 400−500 °C trapped in three different matrices at 4 K: (a) Ar, (b) Xe, and (c) O_2. Lattice vibration in solid oxygen denoted as L. (d) IR spectrum calculated at the UB3LYP/aug-cc-pVTZ level of theory.

Scheme 5. Products of the FVT of Phenylnitrene 1a



these matrices were allowed to anneal at 30 K for several min. Although even small molecules have no tendency for diffusion in argon below 15 K, at temperatures above 20 K, diffusion of O_2 is rapid, allowing bimolecular oxygenation reactions (under similar conditions, carbene **2** reacts completely within minutes).[26] At temperatures above 35 K, argon rapidly evaporates, which limits the useful temperature range to study bimolecular reactions in solid argon to temperatures between 20 and 35 K. However, even prolonged annealing of 4% O_2-doped matrices for several hours at 30−35 K resulted in a loss of less than 5% of **1a**. We finally trapped nitrene **1a** in solid O_2 in the absence of argon (Figure 1c), but no reaction was observed at temperatures up to 20 K when the O_2 matrix starts to degradate. This clearly demonstrates the inertness of **1a** toward O_2 despite both molecules having triplet ground states. The IR spectrum of **1a** in solid O_2 is very similar to that in Ar (Figure 1, Table 1).

We also investigated the photochemistry of **1a** in the O_2 matrix. Irradiation with 450 nm resulted in a decrease of **1a** and the formation of nitrobenzene **8a**. Interestingly, ketenimine **5** is also formed, which indicates that even upon photolysis, the oxidation of **1a** in O_2 is not complete, and small fractions of **1a** undergo the same photochemistry as in rare gas matrices.

Because the reaction between **1a** and O_2 shows a substantial activation barrier, higher temperatures than 20 K are required to induce this reaction under the conditions of matrix isolation. Therefore, O_2-doped xenon matrices, which can be warmed to 70 K without evaporating the matrix, were used for the oxygenation experiments. If a 4% O_2-doped xenon matrix containing **1a** was annealed for 1 h at 40 K, the IR absorptions assigned to **1a** decrease in intensity by approximately 10% and a new compound with the strongest absorptions at 990, 1000, and 1021 cm^{-1} is formed (Figure 2, Table 2). At 50 K, nitrene **1a** decreases after 1 h by 18% and after 12 h by 40%. Prolonged annealing results in only very slow further reactions. In some experiments, the light of the IR source was filtered by a long-pass IR filter blocking light of wavenumbers larger than 2200 cm^{-1}, and additionally, the IR beam was blanked out during the measurements. The qualitative results were the same, from which we conclude that the reaction is not enhanced by IR irradiation.

Table 1. IR Spectroscopic Data of Phenylnitrene 1a Produced by FVT of Phenylazide 3 and Trapping the Products in Ar, Xe, and O_2 at 4 K

	xenon	oxygen	argon		argon (photolysis)[b]	UB3LYP[c]	
mode (sym)	$\tilde{\nu}/cm^{-1}$	$\tilde{\nu}/cm^{-1}$	$\tilde{\nu}/cm^{-1}$	I[a]	$\tilde{\nu}/cm^{-1}$	$\tilde{\nu}/cm^{-1}$	I_{calc}[d]
25 (A1)	1549	1553	1551	22	1552	1586	10.5
24 (B2)	1521	1523	1523	16	1524	1557	2.3
23 (B2)	1424	1427	1426	3	1426	1464	0.8
22 (A1)	1406	1408	1407	2	1408	1446	2.1
21 (B2)	1309	1312	1310	4	1309	1342	0.1
20 (A1)	1282	1289	1282	33	1286	1311	14.8
19 (B2)	1250	1248	1248	3	1250	1269	0.7
17 (A1)	1146	1150	1147	14	1148	1170	4.8
16 (B2)	1075	1079	1078	11	1079	1093	5.8
15 (A1)	1008	1008	1007	5	1008	1027	2.5
12 (A1)	962	964	962	4	964	978	0.8
11 (B1)	884	888	886	4	885	917	4.4
10 (A1)	817	817	817	7	820	833	2.2
8 (B1)	746	749	747	100	746	770	50.7
7 (B1)	654	656	655	62	654	674	34.9
4 (B1)		470	470	4		482	2.0

[a] Intensities in argon relative to the strongest band. [b] **1a** produced by photolysis of **3** in solid argon; data from ref 9. [c] UB3LYP/aug-cc-pVTZ level of theory. [d] Absolute intensities in km/mol.

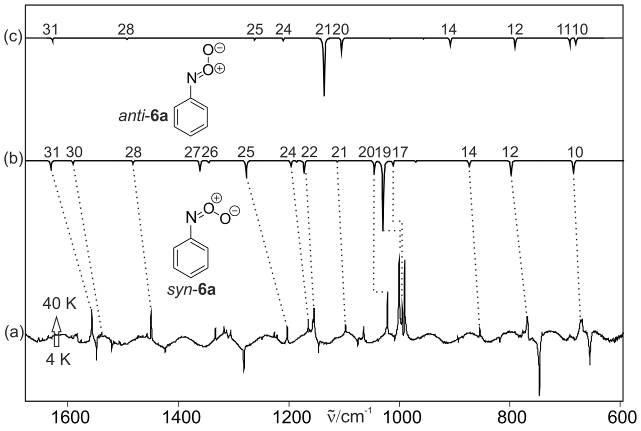


Figure 2. IR spectra of **6a**. (a) Difference spectra after annealing of a 4% O_2-doped xenon matrix containing **1a** from 4 to 40 K. (b) Spectrum of *syn*-**6a** calculated at the B3LYP/aug-cc-pVTZ level of theory, unscaled. Mode numbers on top of the calculated spectra correspond to Table 2. (c) Spectrum of *anti*-**6a** calculated at the B3LYP/aug-cc-pVTZ level of theory, unscaled. Mode numbers on top of the calculated spectra correspond to Tables S4 and S5.

Table 2. IR Spectroscopic Data of Nitroso Oxide 6a

	xenon, 4% O_2[a]			B3LYP[d]		
mode (sym)	$\tilde{\nu}$/ cm^{-1}	I_{rel}[b]	^{18}O shift $\tilde{\nu}$/ cm^{-1}	$\tilde{\nu}$/ cm^{-1}	I_{calc}[e]	^{18}O shift $\tilde{\nu}$/ cm^{-1}
31 (A′)	1586	24	0	1632	26.4	0
30 (A′)	1557	15	0	1591	9.4	0
28 (A′)	1448	18	0	1482	9.7	0
27 (A′)	1333	5	−3	1362	30.4	−1.4
26 (A′)	1318	2	−0.8	1345	7.3	−0.5
25 (A′)	1204	23	−8	1277	47.6	−7.8
24 (A′)	1165	5	−0.5	1196	16.6	−3.6
22 (A′)	1156	5		1172	35.1	−15
21 (A′)	1097	2	−0.5	1112	3.2	−1
	1064	5	−20			
20 (A′)	1021	15	−4	1045	36.3	−1.5
19 (A′)	1000 990	100 76	−52	1030	201.2	−53
17 (A′)	994	2	−2	1011	13.6	0
14 (A′)	854	4	−10	874	18.2	−12
12 (A″)	766	13	0	798	42.5	−0.5
11 (A′)				752[c]	0.4[c]	−10[c]
10 (A″)	671	5	0	684	36.4	0
3 (A′)				249[c]	0.9[c]	−5[c]

[a] O_2-doped Xe (4%) at 4 K. [b] Intensities relative to the strongest band. [c] Anharmonic calculated frequencies at the B3LYP/cc-pVTZ level of theory. [d] B3LYP/aug-cc-pVTZ level of theory. [e] Absolute intensities in km/mol.

Bimolecular reactions in solid matrices not only depend on the intrinsic (gas phase) activation barriers but also on the diffusion of the components and on the local matrix surroundings (matrix sites), and therefore, the kinetics of such systems cannot be evaluated in a meaningful way. Because no reaction of **1a** is found in solid oxygen at 20 K, where diffusion is not necessary, we conclude that the reaction between **1a** and O_2 has an intrinsic activation barrier.

The product of the oxygenation of **1a** in solid xenon proved to be photolabile, and 450 nm irradiation resulted in complete bleaching and the formation of nitrobenzene **8a**, which was identified by comparison with an authentic sample (Figure 3).

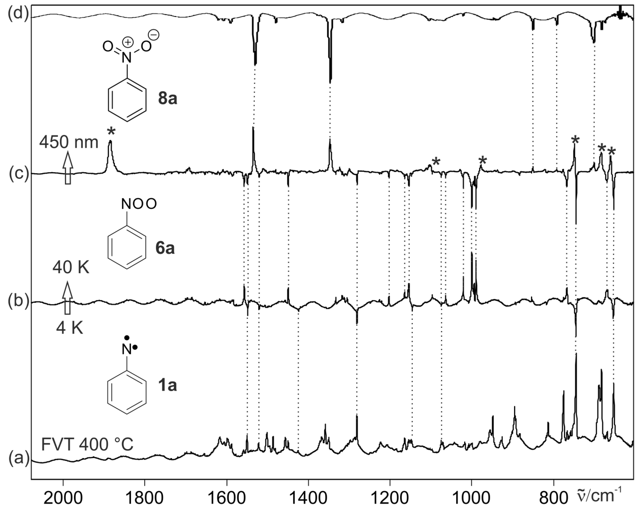


Figure 3. IR spectra showing the reaction of **1a** in 4% O_2-doped Xe. (a) Spectrum obtained after FVT of phenylazide **3** at 400 °C and subsequent trapping of the products in 4% O_2-doped Xe at 4 K. (b) Difference spectrum after annealing at 40 K; bands pointing downward assigned to **1a** are decreasing in intensity, and bands pointing upward assigned to **6a** are appearing. (c) Difference spectrum after irradiation with 450 nm; bands of **6a** decrease in intensity, and bands of nitrobenzene appear concomitantly. Ketenimine **5** is also formed after irradiation (bands marked with asterisks). (d) Authentic matrix isolated sample **8a**.

Therefore, both nitroso oxide **6a** and dioxaziridine **7a** are reasonable structures for the new compound. If $^{18}O_2$ was used in the experiments, the largest ^{18}O isotopic shift was observed for a pair of very strong IR absorptions at 1000 and 990 cm^{-1}, which upon ^{18}O labeling, collapse to a single strong band at 948 cm^{-1}. The large ^{18}O isotopic shift of −52 cm^{-1} clearly indicates an O−O stretching vibration. A similar ^{18}O isotopic shift of −49 cm^{-1} was reported by Inui et al.[18] for nitroso oxide **6c**. The splitting of this vibration into two bands in the ^{16}O isotopomer is most likely due to resonance. Several other bands in the spectrum also show significant ^{18}O isotopic shifts (Table 2).

By comparison of the IR spectrum with the calculated (B3LYP/aug-cc-pVTZ) spectra of *syn*-**6a**, *anti*-**6a**, and **7a**, we conclude that *syn*-**6a** is the main product of the thermal oxygenation of **1a**, whereas **7a** is clearly not formed. The band positions and the isotopic shifts of all bands of *syn*-**6a** are in good agreement with the DFT calculated values (Table 2). For the *syn* conformer, the O−O stretching vibration is predicted at 1030 cm^{-1}, which is in good agreement with the experimental values, whereas for *anti*-**6a**, the O−O stretching is expected at 1135 cm^{-1} (Table 2). The large calculated blue shift of the O−O stretching vibration of *anti*-**6a** compared to *syn*-**6a** makes this vibration diagnostic for the assignment of the conformers and allows us to exclude the formation of significant amounts of *anti*-**6a**. The only indication for the formation of *anti*-**6a** are two IR bands of very low intensity observed at 1125 and 1094 cm^{-1} formed during annealing at 30−35 K together with the bands of *syn*-**6a**. Annealing at higher temperatures increased only the bands of *syn*-**6a**, the assignment of *anti*-**6a** is therefore unconclusive (see SI Figure S10).

The assumption of a resonance causing the splitting of the $^{16}O-^{16}O$ str. vibration is supported by the fact that modes 19 and 20 have the same symmetry, A′, and are close in energy, providing favorable conditions for resonance. An alternative explanation can be found by calculating the anharmonic spectrum at the B3LYP/cc-pVTZ level of theory (Table S6). A combination band between the fundamental vibrations at 752 and 249 cm^{-1} (both A′) is predicted at 1000 cm^{-1}, which is close to the O−O str. vibration calculated at 1016 cm^{-1} (all values referring to the anharmonic calculation). A resonance also explains the large effect of isotopic substitution on the splitting, which is not expected for matrix site effects.

Irradiation of matrices containing *syn*-**6a** under various conditions did not produce the *anti* conformer. The only photochemical reaction observed was the formation of nitrobenzene **8a** and ketenimine **5** (from remaining **1a**).

CONCLUSIONS

FVT of phenylazide **3** is highly efficient to produce clean matrices of phenylnitrene **1a** with only small amounts of rearranged products **5** or **10**. These matrices are therefore ideally suited for studying bimolecular reactions, such as the reaction with O_2. Although reactions of triplet carbenes with O_2 to form carbonyl *O*-oxides show essentially no activation barriers, nitrene **1a** reacts extremely slowly in O_2-doped argon even after prolonged annealing at 30−35 K. Most striking is the lack of thermal reactivity of **1a** in solid O_2, which clearly demonstrates the much lower reactivity of triplet nitrenes compared to triplet carbenes. This observation is in accordance with the activation barrier of 4.3 kcal/mol determined in flash photolysis experiments.[20] Even photochemical excitation of **1a** results only partially in the reaction with O_2 (formation of nitrobenzene **8a**), whereas some **1a** rearranges to **5**, indicating also for the excited state of **1a** a low reactivity with O_2. The observed oxygenation of **1a** during irradiation might be due to hot ground state reactivity, but we have no direct experimental evidence for this hypothesis.

Gritsan and Bally et al. reported that the reaction of **1d** with O_2 results in the formation of both *syn* and *anti* aminophenylnitroso oxide **6d**, which could be interconverted by irradiation with selected wavelengths.[19] A similar behavior was observed for nitrophenylnitroso oxide **6c**.[18] In our experiments, the *syn* conformer of **6a** is formed almost exclusively, and photolysis under various conditions exclusively results in the rearrangement to nitrobenzene **8a**. At the B3LYP/aug-cc-pVTZ level of theory, the *syn* conformer is predicted to be energetically favored by ∼1 kcal/mol compared to the *anti* conformer, which might explain the preference for the *syn* conformer observed in our experiments. However, similar energy differences were calculated for other derivatives of **6**, and therefore, it remains unclear why only *syn*-**6a** is observed in our experiments. In summary, the generation of **1a** via FVT is highly efficient and clean and allows for studying the oxygenation of the nitrene in O_2-doped Xe at cryogenic temperatures.

EXPERIMENTAL SECTION

Matrix isolation experiments were performed by standard techniques[27] using a closed-cycle helium cryostat at 4−50 K. For IR measurements, matrices were deposited on top of a cold CsI window. Matrix infrared spectra were recorded with a FTIR spectrometer using a standard resolution of 0.5 cm^{-1} in the range of 400−4000 cm^{-1}. Phenylnitrene **1a** was generated by FVT of azide **3** using a quartz tube of 8 mm diameter and an 80 mm heating zone; FVT temperatures between 400 and 500 °C were used. For irradiations of matrix-isolated species, a low-pressure mercury lamp (254 nm) and LEDs (450 and 365 nm) were used.

Phenylazide **3** was synthesized starting from aniline according to a literature procedure.[28] For additional purification, a chromatographic column using neutral aluminum oxide, deactivated from stage 1 to stage 4, and a 5:1 mixture of pentane and MTBE as eluent were used.

IR (Ar, 4 K) $\tilde{\nu}$ (cm^{-1}) (%): 462.7 (3), 491.9 (8), 516.8 (2), 537.0 (12), 672.0 (31), 687.0 (17), 749.8 (52), 811.0 (6), 820.4 (2), 893.9 (10), 1004.0 (1), 1027.8 (3), 1077.6 (5), 1102.0 (7), 1130.4 (2), 1137.1 (3), 1176.0 (7), 1185.0 (4), 1275.3 (8), 1281.7 (18), 1289.5 (5), 1299.0 (59), 1305.7 (18), 1345.6 (9), 1459.3 (3), 1468.2 (4), 1491.8 (2), 1496.6 (49), 1590.8 (7), 1593.1 (2), 1600.6 (35), 1622.0 (8), 1716.0 (4), 1786.0 (2), 1852.0 (2), 1871.0 (4), 1934.4 (4), 1943.0 (7), 1950.0 (11), 1969.0 (30), 2089.2 (26), 2101.8 (41), 2110.8 (9), 2135.9 (100), 2156.6 (2), 2165.8 (3), 2266.2 (2), 2412.0 (13), 2428.0 (13), 2576.0 (4), 3040.0 (13), 3086.0 (18), 3108.0 (12).

Nitrobenzene **8a** was purchased and deposited without further purification.

IR (Xe, 4 K) $\tilde{\nu}$ (cm^{-1}) (%): 674.4 (3), 682.4 (5), 701.8 (43), 792.2 (8), 850.4 (10), 1021.6 (3), 1068.5 (2), 1094.1 (2), 1104.0 (3), 1317.0 (5), 1346.1 (79), 1479.4 (4), 1530.0, 1533.5 (100), 1590.8 (6), 1608.4 (3), 1620.8 (4).

Computational Methods. All calculations were carried out with the Gaussian 09[29] suite of programs. Optimized geometries and vibrational frequencies of all species were calculated at B3LYP[30−32] level of theory employing the Dunning's correlation consistent basis set,[33,34] aug-cc-pVTZ. Tight convergence criteria for gradients and an integration grid having 99 radial shells per atom and 590 angular points per shell were used. A spin-unrestricted formalism was used for the triplet phenylnitrene. For the *syn* isomer, the frequencies were also calculated using the anharmonic approximation included in Gaussian09 at the B3LYP/cc-pVTZ level of theory.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01263.

Calculated geometries and frequencies, matrix IR spectra showing products of irradiations, and FVT including ^{18}O-labeled species (PDF)

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Notes

The authors declare no competing financial interest.

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