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Generation of Oxynitrenes and Confirmation of Their Triplet Ground States

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Abstract: New sulfoximine- and phenanthrene-based photochemical precursors to oxynitrenes have been developed. These precursors have been used to examine the chemistry and spectroscopy of oxynitrenes. The first EPR spectra of oxynitrenes are reported and are consistent with their triplet ground states. Additional support for the triplet ground state of oxynitrenes is provided by trapping and reactivity studies, nanosecond time-resolved IR investigations, and computational studies.

Introduction

Although the parent oxynitrene (HON) is an important intermediate in combustion and atmospheric chemistry,[1,2] only relatively limited experimental investigations of oxynitrenes have been reported,[3−15] in contrast to the more thoroughly studied carbon- and nitrogen-substituted nitrenes.[16−20] (Limited reports of sulfur-substituted nitrenes have also appeared.[21−31]) In fact, direct observations of oxynitrene intermediates (RON, R = H, Cl, Br, or CN) via low-temperature matrix IR spectroscopy have only recently been reported.[12−15] We encountered oxynitrene intermediates in our study of the photochemistry of O^2-substituted diazeniumdiolates[32] during the course of our development of novel photochemical precursors to nitric oxide (NO).[33−35]

Oxynitrenes have been generated by the oxidation of *O*-alkylhydroxylamines[3−11,36] and by base-catalyzed decomposition of *N*-sulfonyl-*O*-alkylhydroxylamines.[4,7] (Analogous oxida-

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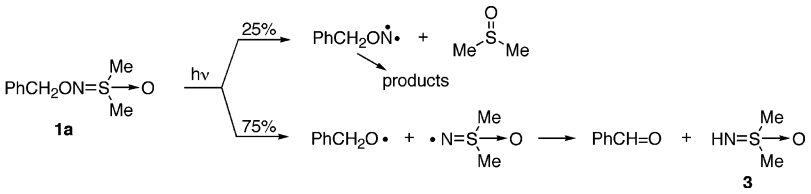
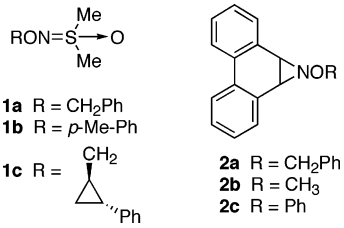
Scheme 1



tion reactions of the corresponding amino compounds have been used to generate aminonitrenes[19,37−40] and sulfenylnitrenes.[23,24]) In the absence of trapping reagents, oxynitrenes undergo rearrangement reactions to form nitroso compounds that tautomerize (when possible) to oximes. Although evidence for oxynitrene intermediates in the above studies has been inferred by alkene trapping to form *N*-alkoxyaziridines, the intermediacy of oxynitrenes in these reactions has been questioned.[6,7]

N-Alkoxyaziridine trapping products generated by oxidation of *O*-alkylhydroxylamines in the presence of *cis*-2-butene or *trans*-2-butene have been found to be formed nonstereospecifically.[7] This observation, together with the assumption (based on analogy with aminonitrenes and semiempirical calculations[36]) that oxynitrenes have singlet ground states, led to the conclusion that oxynitrene intermediates are not likely formed in the oxidation reaction. However, recent high-level calculations indicate that HON is a ground-state triplet by 15−20 kcal/mol,[41−47] consistent with the above trapping studies. Recently, Maier and co-workers generated HON (and several isotopomers) in low-temperature argon matrixes by photolysis of matrix-isolated nitroxyl (HN═O) and concluded that the observed IR spectrum fits much better to that calculated (B3LYP/6-311++G** and QCISD/6-311++G**) for triplet HON compared with that of singlet HON.[14]

Alternative precursors to amino- and sulfenylnitrenes include sulfoximine derivatives[26,38,48,49] and benzonorbornadiene derivatives.[25,40,50,51] The latter precursors are analogous to recently reported carbene precursors that extrude an aromatic compound upon photolysis.[52−58] To investigate the fundamental chemistry of oxynitrenes by time-resolved or low-temperature spectroscopic methods, a general, efficient photochemical precursor is required. Thus, on the basis of the work described above, we have begun our investigations of oxynitrenes with previously unreported sulfoximine derivatives **1** as well as phenanthrene derivatives **2**, which have been reported,[59] but whose photochemistry has not been previously investigated.



Results and Discussion

Product Analysis. Products of photolysis were preliminarily identified by GC/MS and then confirmed and quantified by HPLC and NMR spectroscopy. As has been analogously found for *N*-(arylsulfonyl)sulfoximines,[60,61] the major photochemical pathway for sulfoximines **1** is cleavage of the O−N bond (ca. 75%), rather than formation of oxynitrene and dimethyl sulfoxide (DMSO) (ca. 25%). For example, photolysis (Rayonet, 254 nm) of **1a** yields only 25% DMSO, but significant amounts of benzaldehyde and *S*,*S*-dimethylsulfoximine (**3**) (Scheme 1). Control experiments indicate that sulfoximine **3** is stable to the photolysis conditions, indicating that the observed DMSO is not formed via secondary photolysis.

Photolysis (Rayonet, 300 nm) of phenanthrene-releasing precursors **2**, on the other hand, provides phenanthrene in essentially quantitative yield (97−100%) along with very high yields of oxynitrene-derived products, which, as shown in Scheme 2 for benzyl derivative **2a**, are strongly dependent on the presence of oxygen.

Trapping studies with benzyloxynitrene and phenoxynitrene precursors **2a** and **2c**, respectively, were performed using an alkene (*cis*-2-butene) or H-atom donor (1,4-cyclohexadiene). No trapping is observed with **2a**; however, photolysis of **2c** in neat *cis*-2-butene, to yield both *cis*- and *trans*-*N*-phenoxy-2,3-dimethylaziridine, and in neat 1,4-cyclohexadiene, to yield *O*-phenylhydroxylamine, strongly suggests triplet reactivity. (The difference in reactivity between benzyloxynitrene and phenoxynitrene is discussed further below.)

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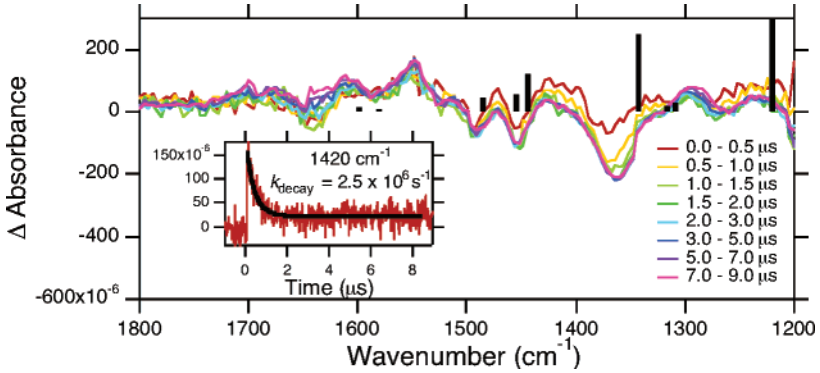


Figure 1. TRIR difference spectra averaged over the time scales indicated following laser photolysis (266 nm, 5 ns, 2 mJ) of a solution of phenanthrene-releasing precursor **2a** in argon-saturated acetonitrile-d_3 overlaid with bars representing B3LYP/6-31G*-calculated IR frequencies (scaled by 0.96) and relative intensities of triplet benzyloxynitrene **4**. The inset shows the kinetics observed at 1420 cm^{-1}. Negative signals are due to depletion of reactant, and positive signals are due to the formation of new transients or products.

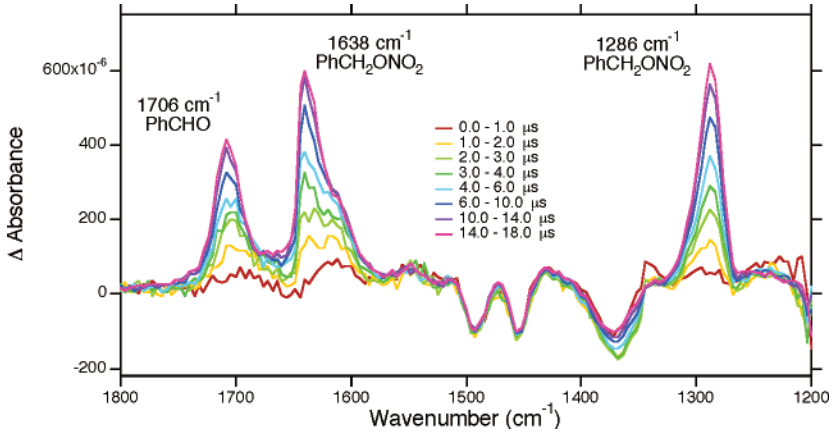
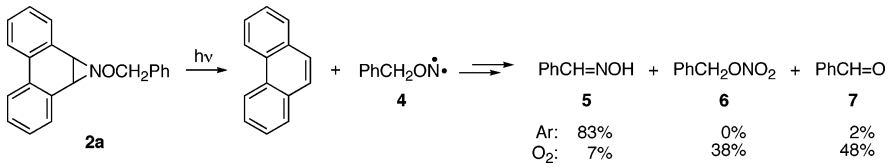


Figure 2. TRIR difference spectra averaged over the time scales indicated following laser photolysis (266 nm, 5 ns, 2 mJ) of a solution of phenanthrene-releasing precursor **2a** in oxygen-saturated acetonitrile-d_3. Negative signals are due to depletion of reactant, and positive signals are due to the formation of new transients or products.

Scheme 2



Time-Resolved IR Studies. Reaction product analyses were supported by nanosecond time-resolved infrared (TRIR) investigations. After 266 nm laser photolysis of the phenanthrene-releasing precursor **2a** in argon-saturated acetonitrile-d_3 (which lacks strong C−H bending modes in the spectral region of interest), a broad, weak signal ($k_{decay} = 2.5 \times 10^6\ s^{-1}$) attributed to triplet benzyloxynitrene **4** is observed from 1330 to 1450 cm^{-1} (overlapping with precursor depletion bands) in reasonable agreement with B3LYP/6-31G* calculations (Figure 1). In oxygen-saturated solutions, this signal is completely quenched while new and intense IR bands assigned to benzyl nitrate (1286 and 1638 cm^{-1}) and benzaldehyde (1706 cm^{-1}) are observed (Figure 2). Although we are unable to detect TRIR signals attributable to methoxynitrene under argon, analogous TRIR data in oxygen-saturated acetonitrile-d_3 (i.e., formation of formaldehyde and methyl nitrate) are observed upon 266 nm laser photolysis of the phenanthrene-releasing precursor **2b** (Figure 3).

On the basis of the observation that benzyloxynitrene **4** is completely quenched by millimolar concentrations of oxygen, we estimate that the rate constant for oxynitrene reaction with oxygen is on the order of $10^9\ M^{-1}\ s^{-1}$. (The concentration of oxygen in saturated acetonitrile solutions is 9.1 mM.[62]) This rate constant is consistent with that for a triplet carbene reaction with oxygen,[63−67] but is in stark contrast to rate constants for reaction of arylnitrenes with oxygen, which are known to be very sluggish, typically near $10^5\ M^{-1}s^{-1}$.[68−73]

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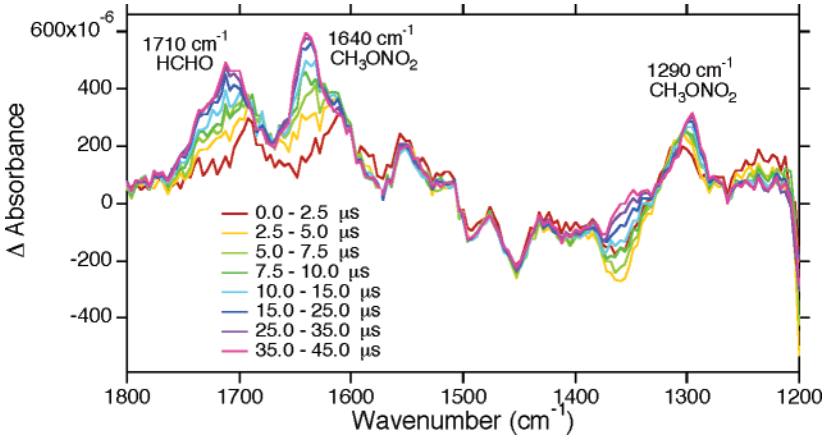


Figure 3. TRIR difference spectra averaged over the time scales indicated following laser photolysis (266 nm, 5 ns, 2 mJ) of a solution of phenanthrene-releasing precursor **2b** in oxygen-saturated acetonitrile-d_3. Negative signals are due to depletion of reactant, and positive signals are due to the formation of new transients or products.

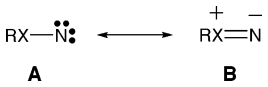
Table 1. Calculated Singlet−Triplet Energy Gaps[a] (kcal/mol) for Heteroatomic Nitrenes (X−N)

computational method	H_2N–N	CH_3HN–N	HO–N	CH_3O–N	HS–N	CH_3S–N
MP2/6-311G**	−10.9	−18.9	23.7	16.8	−0.8	−11.4
CCSD/6-311G**	−11.8	−19.1	20.0	15.4	−1.9	−8.7
MRCISD/6-311G**	−12.1	*b*	20.2	9.4	0.4	*b*
BPW91/cc-pVTZ	−15.1	−20.5	18.4	7.7	−5.0	−10.7
B3LYP/6-311G**	−12.7	−17.7	20.5	15.2	−1.0	−7.0
CBS-QB3	−16.8	−22.2	16.0	11.5	−11.1	−16.1
G2	−17.4	−22.9	14.8	10.1	−12.4	−18.1

[a] Negative values signify that the singlet state is lower in energy. Geometries have been optimized at the specified level for the (closed-shell) singlet and the (open-shell) triplet states. [b] Not determined.

The reaction of oxynitrenes with oxygen has recently been examined by computational methods.[74] It was concluded that the rapid reaction of benzyloxynitrene with oxygen is the result of partial electron transfer in the transition state, followed by rapid collapse of the "ion pair" to form a nitrene oxide that subsequently undergoes a facile rearrangement to a nitrate via a dioxaziridine intermediate. Such a pathway has been proposed previously for oxynitrenes formed from photolysis of O^2-substituted diazenium diolates.[32]

Spin States of Oxynitrenes. When we first encountered oxynitrenes, we anticipated by analogy with aminonitrenes that oxynitrenes would have singlet ground states. As discussed above, however, high-level calculations have recently indicated that HON is a ground-state triplet by 15−20 kcal/mol.[41−47] We addressed the energetics of oxynitrenes, as well as their amino and sulfenyl analogues, by computational methods, and the results are presented in Table 1, with a positive singlet−triplet energy gap (ΔE_{ST}) indicating a triplet ground state. Substitution of the hydrogen in HON by an electron-donating methyl group lowers the singlet nitrene energy relative to the triplet energy in each of the heteroatomic nitrenes investigated. The calculations at the G2 and CBS-QB3 levels are probably the most reliable estimates for the singlet−triplet energy gaps as the singlet states for these nitrenes are well described by a single-reference, closed-shell wave function (see below). Such stabilization can be rationalized in terms of singlet nitrene resonance form **B** and the ability of the X group to donate electron density to the nitrene's N center. Amino and sulfenyl groups are better electron donors and help to stabilize resonance forms, such as **B**, for the singlet state. Oxygen, on the other hand, is less good as an electron donor and thereby favors the triplet state. Charge density difference plots between the singlet and triplet states for these X−N species are provided in the Supporting Information and confirm that the lone pair orbitals on the X donor and the nitrene N's p orbitals are the most important.



Further insight into the origin of the preference for the triplet state of the oxynitrene can be obtained with the following isodesmic reaction:

$$H_2NCH_2O{-}N^{1,3} \rightarrow HOCH_2NH{-}N^{1,3}$$

For this hypothetical reaction, we compute ΔH(0 K) of the reaction to be −37.8 kcal/mol when comparing the singlet nitrenes and only −5.4 kcal/mol for the triplet nitrenes at the CBS-QB3 level. Thus, the more electron-donating amino substituent does stabilize the singlet and triplet nitrenes, but the singlet nitrene is more strongly stabilized by the adjacent amino substituent. This differential substituent effect on the amino- and oxynitrenes provides for the large change in singlet−triplet energy gap (ΔH(0 K)) between H_2NCH_2O−N (+11.1 kcal/mol, favoring the triplet) and $HOCH_2NH$−N (−21.4 kcal/mol, favoring the singlet) at the CBS-QB3 level. These singlet−triplet energy gaps are similar to the values for CH_3NH−N and CH_3O−N in Table 1.

Calculations at the B3LYP/6-311G** level for the nitrene's X−N bond lengths are provided in Table 2 and for other levels in the Supporting Information. Calculated bond lengths for the singlet state are consistently shorter than those in the triplet state, with larger changes observed for amino- and sulfenylnitrenes, which are predicted to have singlet ground states.

We have also examined the relative energies of closed-shell and open-shell singlet states for H_2N−N, HO−N, and HS−N by the MCSCF and MRCISD methods (Table 3). In each case, the closed-shell singlet ($^1A'$) is calculated to be lower in energy relative to the open-shell singlet ($^1A''$) by approximately 50, 15, and 27 kcal/mol, respectively. These results are in contrast to those of phenylnitrene, which is a ground-state triplet by 18

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Table 2. B3LYP/6-311G**-Calculated Nitrene Heteroatom−Nitrogen Bond Lengths[a]

nitrene (X–N)	singlet X–N bond length (Å)	triplet X–N bond length (Å)	Δ(bond length) (singlet – triplet) (Å)
H_2N-N	1.212	1.343	−0.131
CH_3HN-N	1.206	1.355	−0.149
HO−N	1.255	1.324	−0.069
CH_3O-N	1.228	1.310	−0.082
HS−N	1.510	1.668	−0.158
CH_3S-N	1.504	1.650	−0.146

[a] Geometries have been optimized at the B3LYP/6-311G** level for the (closed-shell) singlet and the (open-shell) triplet states.

Table 3. Calculated Relative Energies (kcal/mol) between the $^1A'$ and $^1A''$ States of Heteroatomic Nitrenes (X−N)[a]

	H_2N–N		HO–N		HS–N	
	$^1A'$	$^1A''$	$^1A'$	$^1A''$	$^1A'$	$^1A''$
MCSCF/6-311G**	0.0	53.6	0.0	15.8	0.0	24.4
MRCISD/6-311G**	0.0	45.7	0.0	13.7	0.0	29.1

[a] Geometries have been optimized at the specified level for the (closed-shell) $^1A'$ and the (open-shell) $^1A''$ states (see the Experimental Section for details on the calculations).

kcal/mol, but whose lowest singlet state is the open-shell configuration.[75] However, these results are completely consistent with those reported by Liu et al. for other oxynitrenes.[74]

Low-Temperature ESR Spectroscopy. To confirm experimentally the production of triplet oxynitrenes upon photolysis of phenanthrene-releasing precursors **2a**−**c** and *O*[2]-methyl diazeniumdiolate **8**, these precursors were irradiated in frozen matrixes and examined by low-temperature EPR spectroscopy. The results, which represent the first EPR detection of oxynitrene intermediates, are shown in Figure 4. In each case, two high-field oxynitrene absorptions are observed in the region between 8000 and 10000 G. The zero-field parameters *D* and *E* (Table 4) were derived assuming the *g* value of each nitrene was equal to the free electron value (g_e). Also included in Table 4 are *D* and *E* values previously determined for other representative alkyl-, aryl-, and carbonylnitrenes. Interestingly, our experimentally determined oxynitrene *D* values (1.96, 1.93, and 1.97 cm^{-1}) are all comparable to that derived for imidogen (H−N, $D = 1.86$ cm^{-1})[76] and much larger than that of methylnitrene (CH_3−N, $D = 1.595$ or 1.720 cm^{-1}).[76,77]

Since the *D* value is proportional to the inverse cube of the average distance between the two unpaired electrons,[78] smaller *D* values in nitrenes are usually interpreted to signify greater delocalization of spin density away from the nitrogen atom.[76] Thus, the oxynitrene *D* values presented here suggest very little or no delocalization of electron spin. This observation is consistent with the UMP2/6-311G**-calculated spin density on N (1.764 and 1.719) and on O (0.204 and 0.217) for HO−N and CH_3O−N, respectively. However, the oxynitrene *E* values determined in this work are significantly different from zero, much like those of (*m*-bromophenyl)nitrene or (ethoxycarbonyl)-nitrene (Table 4). Perhaps the repulsive interaction between the oxygen lone pairs and the unpaired electrons on nitrogen serve

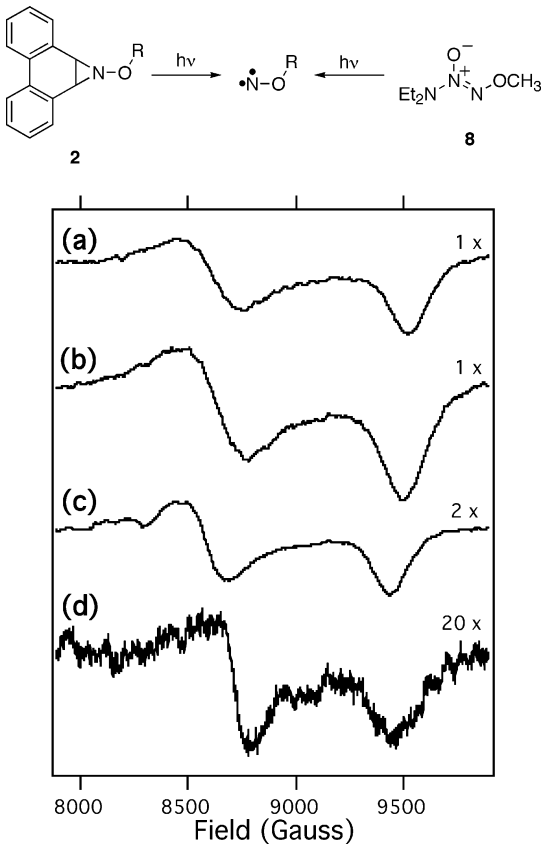

Figure 4. Low-temperature EPR spectra obtained after irradiation at 10 K of the (a) diazenium diolate **8** in methylcyclopentane, (b) methoxynitrene precursor **2b** in methylcyclopentane, (c) phenoxynitrene precursor **2c** in methylcyclohexane, and (d) benzyloxynitrene precursor **2a** in methylcyclohexane.

Table 4. Nitrene EPR Zero-Field Parameters

R (in RO–N)	R′ (in R′–N)	*D* (cm^{-1})	*E* (cm^{-1})	ref
CH_3 (from **8**)		1.96	0.0142	this work
CH_3 (from **2b**)		1.96	0.0147	this work
Ph		1.93	0.0141	this work
CH_2Ph		1.97	0.0118	this work
	H	1.86	0	76
	CH_3	1.595	<0.003	76
		1.720		77
	Ph	0.9978	<0.002	76
	m-BrPh	0.9882	0.0075	76
	EtOC(═O)	1.603	0.0215	76
	Me_3Si	1.57	0	79
	$(PhO)_2P(═O)$	1.541	0.0074	80

to reduce the effective distance between the two unpaired electrons. Such an interaction may also result in a nonsymmetrical distribution of the unpaired electrons, thus leading to an enhanced *E* value. Another potential explanation involves a significant contribution from spin−orbit coupling that makes the *g* values of oxynitrenes significantly different from g_e; thus, inaccurate *D* and *E* are derived since *g* is assumed to be equal to g_e.[76,78]

Oxynitrene to Nitroso Rearrangement. The mechanism of HON (triplet ground state) rearrangement to HN═O (singlet ground state) has been examined in detail by computational methods.[1,2] Mechanistic possibilities include concerted or stepwise (via a H-atom and NO) reactions on either a singlet or a triplet potential energy surface. Results indicate that concerted

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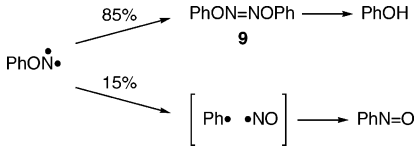
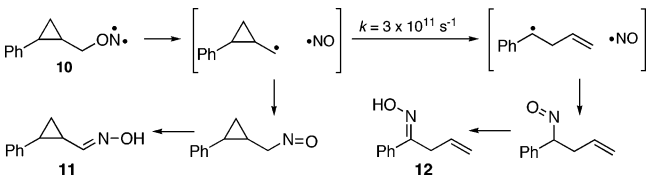
Scheme 3



Scheme 4



rearrangement of HON to HN═O involves a barrier that is higher than the dissociation barrier (to H• + •NO) on the singlet surface.[1,42] On the triplet surface, the concerted rearrangement barrier (to triplet HN═O) is calculated to be higher[1] or comparable[42] to the dissociation barrier. Maier has obtained some evidence for the dissociation mechanism of rearrangement in his low-temperature matrix IR studies of HON.[14]

We reasoned that if the rearrangement does indeed occur stepwise, then the rate of rearrangement should depend on the radical stability. When phenoxynitrene precursor **2c** is photolyzed, we find low yields of nitrosobenzene, which if formed via the stepwise process would be required to proceed through the very unstable phenyl radical (Scheme 3). The major decomposition pathway observed for phenoxynitrene is formation of phenol. We propose that the phenol arises from dimerization of phenoxynitrene to the unstable hyponitrite ester **9**, which subsequently loses nitrogen and forms phenol, as has been proposed previously.[5,81] For comparison, benzyloxynitrene produces rearrangement products (oximes **5**), presumably involving formation of a stabilized benzyl radical, almost exclusively (Scheme 2).

To gain further evidence for a stepwise oxynitrene to nitroso rearrangement, we have also examined by HPLC the products formed from oxynitrene **10** (formed via photolysis of its corresponding sulfoximine precursor **1c**). We find that both oximes **11** and **12** are produced, providing additional evidence for a stepwise rearrangement process, in this case through an intermediate (2-phenylcyclopropyl)carbinyl radical[82] (Scheme 4).

Conclusions

Phenanthrene-releasing precursors **2a**−**c** have been shown to be efficient photochemical precursors to oxynitrenes. These precursors have been used to obtain the first EPR spectra of oxynitrenes, consistent with their triplet ground states. The triplet ground state of oxynitrenes is also reflected in trapping (with oxygen, *cis*-2-butene, and 1,4-cyclohexadiene) and reactivity studies, nanosecond TRIR investigations, and computational studies. In addition, TRIR studies have been used to estimate that the rate constant for the reaction of benzyloxynitrene **4** with oxygen is on the order of 10^9 M^{-1} s^{-1}, consistent with previous computational predictions.[74]

Experimental Section

General Methods. Unless otherwise noted, materials were obtained from Aldrich Chemical Co., Fisher Scientific, or Cambridge Isotope Laboratories and were used without further purification. *O*^{2}-Methyl 1-(*N*,*N*-diethylamino)diazen-1-ium-1,2-diolate (**8**) was kindly provided by Drs. Joseph E. Saavedra and Larry K. Keefer at the NCI in Frederick, MD. Dichloromethane was distilled from phosphorus pentoxide and tetrahydrofuran was distilled from sodium/benzophenone before use. Dimethyl sulfoxide was distilled from calcium hydride under vacuum. ^{1}H NMR spectra were recorded on a Bruker AMX 300 (300 MHz) or a Varian Unity Plus 400 (400 MHz) Fourier transform NMR spectrometer. ^{13}C NMR spectra were recorded on a Varian Unity Plus 400 (100 MHz) Fourier transform NMR spectrometer. Resonances are reported in δ units downfield from the peak for tetramethylsilane. Mass spectra were collected with a VG 70-S mass spectrometer in the fast atom bombardment (FAB) mode or EI/CI mode with sample induction via a direct probe, a Kompact Kratos MALDI instrument, or a Shimadzu QP5050A GC/MS instrument in EI mode with a Shimadzu AOC-20i autosampler. HPLC analysis was performed on one of two systems: (1) a Waters Delta 600 system equipped with a model 6000A pump and a model 2487 dual-wavelength UV detector or (2) a Perkin-Elmer Series 4 HPLC system with a PE85B variable-wavelength detector. GC analysis was performed on an HP5790 with an FID detector equipped with an integrator or a Shimadzu QP5050A GC/MS instrument. Ultraviolet−visible (UV−vis) absorption spectra were obtained using a Hewlett-Packard 8453 diode array spectrometer. Infrared (IR) absorption spectra were obtained using a Bruker IFS 55 Fourier transform infrared spectrometer.

***S*,*S*-Dimethyl-*N*-benzoxysulfoximine (1a).** A solution of freshly prepared *tert*-butyl hypochlorite[83] (3.1 g, 28.5 mmol) in 90 mL of methylene chloride under nitrogen was cooled using a dry ice/chloroform bath. A solution of dimethyl sulfoxide (8.8 g, 113 mmol) in 40 mL of dichloromethane was then added slowly, and the resulting solution was allowed to stir for 1 h. *O*-Benzylhydroxylamine (3.6 g, 29.5 mmol) in 40 mL of dichloromethane was added to this mixture; the solution was allowed to stir for an additional 3 h. This was followed then by the addition of triethylamine (7.25 g, 72 mmol) in 30 mL of dichloromethane. After the addition was complete, the mixture was allowed to warm to room temperature. The mixture was washed with water (5×) and dried with sodium sulfate, and the solvent was removed. The residue was chromatographed on silica gel using 70% ethyl acetate/hexane as an eluent to give 0.90 g of **1a** (15%) as a white solid: ^{1}H NMR ($CDCl_3$) δ 3.06 (6 H, s), 4.87 (2 H, s), 7.38 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 37.44, 79.29, 127.99, 128.28, 128.90, 137.35; MS (FAB) 200 (M + 1), 222 (M + Na); UV−vis (CH_3CN) λ_{max} 210, 260 nm (ϵ_{254} = 380 M^{-1} cm^{-1}).[84]

***S*,*S*-Dimethyl-*N*-(4-methylphenoxy)sulfoximine (1b).** Ethyl *O*-(mesitylsulfonyl)acetohydroxamate (3.0 g, 11 mmol) was dissolved in 6 mL of dioxane, and then 6 mL of perchloric acid (70%) was added in portions, resulting in the formation of a precipitate. Once the perchloric acid addition was complete, the resulting mixture was allowed to stir for 5−10 min. The mixture was then added to ice−water, and the precipitate was filtered and dried to give 1.89 g of *O*-(mesitylsulfonyl)hydroxylamine.[85]

p-Cresol (1.5 g, 13.8 mmol) was dissolved in 20 mL of methanol, and then potassium *tert*-butoxide (1.5 g, 13.3 mmol) was added. The mixture was allowed to stir for 5 min, the methanol was removed, and the residue was taken up in 10 mL of dichloromethane. Then to this was added the freshly prepared *O*-mesitylsulfonylhydroxylamine (1.89 g, 8.8 mmol) in 10 mL of dichloromethane under ice cooling. The mixture was allowed to stir for 1 h, washed with water, and dried with

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sodium sulfate, and the dichloromethane was removed. The residue was chromatographed on silica gel using dichloromethane as an eluent to obtain 0.97 g of *O*-(4-methylphenyl)hydroxylamine (90%): ^{1}H NMR ($CDCl_3$) δ 2.31 (3 H, s), 5.82 (2 H, br s), 7.06 (4 H, m).[86]

A solution of freshly prepared *tert*-butyl hypochlorite[83] (1.3 g, 12 mmol) in 45 mL of methylene chloride under a nitrogen atmosphere was cooled using a dry ice/chloroform bath. A solution of dimethyl sulfoxide (4.4 g, 56 mmol) in 20 mL of dichloromethane was added slowly, and the resulting solution was allowed to stir for 1 h. *O*-(4-Methylphenyl)hydroxylamine (1.2 g, 9.7 mmol) in 20 mL of dichloromethane was subsequently added, and the resulting solution was allowed to stir for an additional 3 h. This was followed by the addition of triethylamine (2.9 g, 29 mmol) in 15 mL of dichloromethane. Once the addition was complete, the mixture was allowed to warm to room temperature. The mixture was diluted with 40 mL of dichloromethane, washed with water (5×), and dried with sodium sulfate, and the solvent was removed. The residue was chromatographed on silica gel using 70% ethyl acetate/hexane as an eluent to give 0.41 g of **1b** (21%) as a light brown solid: ^{1}H NMR ($CDCl_3$) δ 2.28 (3 H, s), 3.21 (6 H, s), 7.06 (4 H, s); ^{1}H NMR (CD_3CN) δ 2.28 (3 H, s), 3.12 (6 H, s), 7.03 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 20.58, 37.57, 113.74, 129.61, 130.54, 159.59; MS (FAB) *m*/*z* 199 (M), 222 (M + Na); UV−vis (CH_3CN) λ_{max} 225, 280 nm ($\epsilon_{254} = 7446$ M^{-1} cm^{-1}).[84]

***S,S*-Dimethyl-*N*-[(2-phenylcyclopropyl)methoxy]sulfoximine (1c).** Lithium aluminum hydride (0.772 g, 20.3 mmol) was added to a flame-dried round-bottom flask followed by 45 mL of tetrahydrofuran. To this slurry was added 2-phenylcyclopropanecarboxylic acid (3.00 g, 18.5 mmol) in 45 mL of tetrahydrofuran. The mixture was allowed to stir at room temperature for 2.5 h and then at a gentle reflux overnight. The reaction was quenched with addition of methanol (2 mL), water (2 mL), and 10% aqueous sodium hydroxide (2 mL). The solids were then filtered, and the solvent was removed. The residue was taken up in ethyl ether, washed with water, and dried over magnesium sulfate, and the solvent was removed to obtain (2-phenylcyclopropyl)methanol (1.90 g, 70%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.96 (2 H, m), 1.46 (1 H, m), 1.82 (1 H, m), 3.62 (2 H, m), 7.08 (2 H, m), 7.18 (1 H, m), 7.27 (2 H, m).

This alcohol (1.60 g, 11 mmol) was combined with *N*-hydroxyphthalimide (1.80 g, 11 mmol), and triphenylphosphine (2.88 g, 11 mmol) in 50 mL of tetrahydrofuran, followed by the dropwise addition of diisopropyl azodicarboxylate (2.43 g, 12 mmol). The mixture was then allowed to stir for 2 days. The solvent was removed, and the residue was chromatographed on silica gel using 15% ethyl acetate/petroleum ether mixture as an eluent. The product was recrystallized using dichloromethane/petroleum ether to provide 2-[(2-phenylcyclopropyl)methoxy]isoindole-1,3-dione as colorless needles (0.83 g, 26%): ^{1}H NMR ($CDCl_3$) δ 1.04 (2 H, m), 1.63 (1 H, m), 1.90 (1 H, m), 4.23 (2 H, m), 6.98 (2 H, m), 7.18 (3 H, m), 7.75 (4 H, m).[87]

This dione (1.3 g, 4 mmol) was dissolved in 15 mL of ethanol and combined with 0.50 mL of hydrazine hydrate. This solution was heated at reflux for 1 h and then cooled to room temperature. The solids that formed were dissolved with 3% aqueous sodium carbonate solution (100 mL), and then the product was extracted with ethyl ether. The ethyl ether was removed to obtain *O*-[(2-phenylcyclopropyl)methyl]-hydroxylamine as a colorless oil.[87]

A solution of freshly prepared *tert*-butyl hypochlorite[83] (0.80 g, 7.4 mmol) in 20 mL of methylene chloride was cooled using a dry ice/chloroform bath under nitrogen, and a solution of dimethyl sulfoxide (2.2 g, 28 mmol) in 15 mL of dichloromethane was added slowly; the resulting solution was allowed to stir for 1 h. Then freshly prepared *O*-[(2-phenylcyclopropyl)methyl]hydroxylamine (0.65 g, 4.0 mmol) in 20 mL of dichloromethane was added, and the resulting solution was allowed to stir for an additional 3 h. This was followed then by the addition of triethylamine (0.73 g, 7.2 mmol) in 15 mL of dichloromethane. Once the addition was complete, the mixture was allowed to warm to room temperature. The mixture was diluted with 40 mL of dichloromethane, washed with water (5×), and dried with sodium sulfate, and the solvent was removed. The residue was chromatographed on silica gel using 70% ethyl acetate/hexane as an eluent to give 0.124 g (13%) of **1c** as an off-white solid: ^{1}H NMR ($CDCl_3$) δ 0.99 (2 H, t, $J = 5.4$ Hz), 1.53 (1 H, m), 1.86 (1 H, m), 3.08 (6 H, s), 3.84 (2 H, m), 7.07−7.27 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 14.2, 21.6, 22.0, 37.4, 80.8, 125.5, 125.8, 128.2, 142.6; MS (EI) *m*/*z* 131 (95), 91 (100); UV−vis (CH_3CN) λ_{max} 195, 220 nm ($\epsilon_{254} = 430$ M^{-1} cm^{-1}).

1a,9b-Dihydro-1-benzoxy-1*H*-phenanthro[9,10-*b*]azirine (2a). 2,2′-Biphenyldicarboxaldehyde[88] (2.32 g, 10.9 mmol) was dissolved in 25 mL of pyridine with 3 Å molecular sieves, and then to this was added *O*-benzylhydroxylamine hydrochloride (1.74 g, 10.9 mmol). The mixture was allowed to stir for 16 h and then was taken up in ethyl ether. This mixture was washed with water, 10% hydrochloric acid solution (4×), and a saturated sodium chloride solution. The organic layer was dried over magnesium sulfate, and the solvent was removed. The residue was purified by column chromatography on silica gel using 5% ethyl acetate/hexane as an eluent to give biphenyl-2,2′-dicarboxaldehyde mono(*O*-benzyloxime) as a colorless oil (1.1 g, 32%): ^{1}H NMR ($CDCl_3$) δ 5.13 (2 H, s), 7.25−7.60 (11 H, m), 7.87 (1 H, s), 8.00 (2 H, m), 9.76 (1 H, s).[59]

This oxime (2.40 g, 7.6 mmol) was dissolved in 20 mL of methanol followed by the addition of *p*-toluenesulfonic acid hydrazide (1.55, 8.3 mmol). The mixture was allowed to stir for 16 h, and the precipitate that was formed was filtered and dried to give 3.4 g (92%) of 4-methylbenzenesulfonic acid [[2′-[(benzoxyimino)methyl][1,1′-biphenyl]-2-yl]methylene]hydrazide as a white powder: ^{1}H NMR ($CDCl_3$) δ 2.40 (3 H, s), 5.09 (2 H, s), 7.11 (2 H, m), 7.28−7.38 (11 H, m), 7.62 (1 H, s), 7.79 (1 H, s), 7.81 (2 H, d, $J = 8.3$ Hz), 7.97 (2 H, m).[59]

This hydrazide (3.4 g, 7.0 mmol), dissolved in 35 mL of tetrahydrofuran, was added under nitrogen to a slurry of sodium hydride (0.18 g, 7.5 mmol) and 5 mL of tetrahydrofuran. Once the addition was complete, the mixture was allowed to stir for 2 days. The tetrahydrofuran was removed, and the reaction mixture was taken up in dichloromethane and washed with water. The organic layer was dried over sodium sulfate, and then the solvent was removed. The residue was purified by column chromatography on silica gel using 5% ethyl acetate/hexane to obtain 0.87 g (42%) of **2a**: ^{1}H NMR ($CDCl_3$) δ 3.70 (2 H, s), 4.85 (2 H, s), 7.27−7.37 (11 H, m), 7.94 (2 H, d, $J = 6.4$ Hz); MS (FAB) *m*/*z* 300 (M + 1), 322 (M + Na); UV−vis (CH_3CN) λ_{max} 210, 250, 280, 310 nm ($\epsilon_{300} = 4664$ M^{-1} cm^{-1}); IR (neat) 3061, 3033, 2912, 2841, 1488, 1454, 1354, 1259, 1240, 1202, 1152, 1012 cm^{-1}.[59]

1a,9b-Dihydro-1-methoxy-1*H*-phenanthro[9,10-*b*]azirine (2b). 2,2′-Biphenyldicarboxaldehyde[88] (2.75 g, 12.9 mmol) was dissolved in 20 mL of pyridine with 3 Å molecular sieves, and then *O*-methylhydroxylamine hydrochloride (0.98 g, 11.8 mmol) was added. The mixture was allowed to stir for 3 days and then taken up in ethyl ether. The ether layer was washed with water, 10% hydrochloric acid solution (4×), and a saturated sodium chloride solution. The organic layer was dried over sodium sulfate, and the solvent was removed. The residue was purified by column chromatography on silica gel using 5% ethyl acetate/hexane to give biphenyl-2,2′-dicarboxaldehyde mono-(*O*-methyloxime) as a colorless oil (1.0 g, 35%): ^{1}H NMR ($CDCl_3$) δ 3.90 (3 H, s), 7.29 (2 H, m), 7.44−7.64 (4 H, m), 7.78 (1 H, s), 8.02 (2 H, m), 9.76 (1 H, s).[59]

Biphenyl-2,2′-dicarboxaldehyde mono(*O*-methyloxime) (1.0 g, 4.1 mmol) was dissolved in 20 mL of methanol, and then *p*-toluenesulfonic acid hydrazide (0.85, 4.5 mmol) was added. The mixture was allowed to stir for 48 h, and the precipitate that was formed was filtered and

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dried to give 1.15 g (69%) of 4-methylbenzenesulfonic acid [[2′-[(methoxyimino)methyl][1,1′-biphenyl]-2-yl]methylene]hydrazide as a white powder: ^{1}H NMR ($CDCl_3$) δ 2.42 (3 H, s), 3.86 (3 H, s), 7.15 (2 H, m), 7.31 (2 H, d, J = 8.0 Hz), 7.39 (4 H, m), 7.54 (1 H, s), 7.65 (1 H, s), 7.81 (2 H, d, J = 8.3 Hz), 7.97 (2 H, m).[59]

This hydrazide (1.2 g, 2.8 mmol) was dissolved in 15 mL of tetrahydrofuran and added under nitrogen to a slurry of sodium hydride (0.074 g, 3.1 mmol) and 10 mL of tetrahydrofuran. Once the addition was complete, the mixture was allowed to stir for 2 days. The tetrahydrofuran was removed, and the reaction mixture was taken up in dichloromethane and washed with water. The organic layer was dried over sodium sulfate, and then the solvent was removed. The residue was purified by column chromatography on silica gel using 5% ethyl acetate/hexane to obtain 0.20 g (32%) of **2b**: ^{1}H NMR ($CDCl_3$) δ 3.65 (3 H, s), 3.73 (2 H, s), 7.32−7.38 (4 H, m), 7.59 (2 H, m), 7.97 (2 H, d, J = 7.6 Hz); MS (MALDI) m/z 223 (M), 224 (M + 1); UV−vis (CH_3CN) λ_{max} 217, 250, 280, 310 nm (ϵ_{300} = 4545 M^{-1} cm^{-1}); IR (neat) 3059, 3028, 2982, 2935, 2893, 2853, 1490, 1467, 1452, 1433, 1378, 1260, 1240, 1202, 1164, 1043, 1015 cm^{-1}.[59]

1a,9b-Dihydro-1-phenoxy-1*H*-phenanthro[9,10-*b*]azirine (2c). 2,2′-Biphenyldicarboxaldehyde[88] (3.43 g, 16.2 mmol) was dissolved in 20 mL of pyridine with 3 Å molecular sieves, and then *O*-phenylhydroxylamine hydrochloride (1.77 g, 16.2 mmol) was added. The mixture was allowed to stir for 15 h and then was taken up in ethyl ether. This mixture was washed with water, 10% hydrochloric acid solution (4×), and a saturated sodium chloride solution. The organic layer was dried over sodium sulfate, and the solvent was removed. The residue was purified by column chromatography on silica gel using 10% ethyl acetate/hexane as an eluent to give biphenyl-2,2′-dicarboxaldehyde mono(*O*-phenyloxime) as a colorless oil (2.8 g, 57%): ^{1}H NMR ($CDCl_3$) δ 7.12 (3 H, m), 7.31 (4 H, m), 7.50−7.68 (4 H, m), 8.12 (2 H, m), 8.17 (1 H, s), 9.83 (1 H, s).[59]

Biphenyl-2,2′-dicarboxaldehyde mono(*O*-phenyloxime) (2.8 g, 9.29 mmol) was dissolved in 20 mL of methanol, and then *p*-toluenesulfonic acid hydrazide (1.9 g, 10.2 mmol) was added. The mixture was allowed to stir for 48 h, and the precipitate that was formed was filtered and dried to give 3.4 g (78%) of 4-methylbenzenesulfonic acid [[2′-[(phenoxyimino)methyl][1,1′-biphenyl]-2-yl]methylene]hydrazide as a white powder: ^{1}H NMR ($CDCl_3$) δ 2.36 (3 H, s), 7.02−7.30 (9 H, m), 7.45 (4 H, m), 7.52 (1 H, s), 7.77 (2 H, d, J = 8.4 Hz), 8.01 (1 H, s), 8.03 (2 H, m).[59]

This hydrazide (3.4 g, 7.2 mmol) was dissolved in 15 mL of tetrahydrofuran and added under nitrogen to a slurry of sodium hydride (0.174 g, 7.2 mmol) in 10 mL of tetrahydrofuran. Once the addition was complete, the mixture was allowed to stir for 2 days. The tetrahydrofuran was removed, and the reaction mixture was taken up in dichloromethane and washed with water. The organic layer was dried over sodium sulfate, and then the solvent was removed. The residue was purified by column chromatography on silica gel using 5% ethyl acetate/hexane to obtain 0.67 g (33%) of **2c**: ^{1}H NMR ($CDCl_3$) δ 4.03 (2 H, s), 7.03 (3H, m), 7.26 (2 H, m), 7.36−7.43 (4 H, m), 7.62 (2 H, d, J = 7.4 Hz), 8.02 (2 H, d, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 49.15, 113.68, 121.42, 123.55, 128.44, 128.64, 129.01, 129.39, 130.81, 131.64, 159.18; MS (MALDI) m/z 285 (M); UV−vis (CH_3CN) λ_{max} 200, 215, 250, 280, 310 nm (ϵ_{300} = 4717 M^{-1} cm^{-1}); IR (neat) 3072, 3037, 3021, 1598, 1588, 1490, 1480, 1454, 1224, 1164, 1074, 1022 cm^{-1}.[59]

***S,S*-Dimethylsulfoximine (3).** To a mixture of dimethyl sulfoxide (2.2 g, 28 mmol), 5 mL of concentrated sulfuric acid, and 20 mL of dichloromethane was added sodium azide (2.0 g, 31 mmol) using a powder addition funnel over 1 h. The mixture was allowed to stir for 16 h. The mixture was poured into ice−water and neutralized with sodium bicarbonate, and the solvent was removed. Ethanol was added to the residue, and the solids that formed were filtered (2×). The ethanolic solutions were combined, and the ethanol was removed. The residue was then heated with an air bath at 60 °C under reduced pressure to remove dimethyl sulfoxide: ^{1}H NMR ($CDCl_3$) δ 3.08 (6 H, s); ^{1}H NMR (CD_3CN) δ 2.95 (6 H, s); MS (EI) m/z 93 (90), 78 (100), 60 (79), 46 (70); IR (neat) 3270, 1211, 1045 cm^{-1}.[89]

***syn*- and *anti*-Benzaldehyde Oximes 5.** The *syn*-benzaldehyde oxime is commercially available (Aldrich), and the *anti*-benzaldehyde oxime can be synthesized from the *syn*-oxime.[90] In a three-neck flask, under nitrogen, equipped with a reflux condenser and a tube to introduce hydrochloric acid gas, *syn*-benzaldehyde oxime (2.42 g, 20 mmol) was dissolved in 12 mL of benzene. The mixture was brought to reflux, then heating was stopped, and the flow of hydrochloric acid gas was started. After approximately 5 min a precipitate started to form, and at this point the flow of hydrochloric acid gas was discontinued. The mixture was cooled with an ice bath. The solids were collected by filtration and then washed with benzene and petroleum ether. To a slurry of the solids in 20 mL of ethyl ether under ice cooling was added a precooled solution of sodium hydroxide (15 mL, 2.66 M), and the solids soon dissolved. Once the solids dissolved, a solution of ammonium chloride (4.0 g, 75 mmol) in 15 mL of water was added. Solid precipitated and within 1 min went back into solution. The aqueous and organic layers were then separated, and the aqueous layer was extracted again with ethyl ether. The organic layers were dried over $MgSO_4$, and the solvent was removed. The residue was treated with petroleum ether, and the solids were then filtered to give 1.05 g (43%) of the *anti*-oxime: ^{1}H NMR (CD_3CN) δ 7.34 (1 H, s), 7.44 (3 H, m), 7.93 (2 H, m), 9.29 (1 H, s); mp 121−122.5 °C (lit.[90] mp 129.5−130 °C).

Benzyl Nitrate (6). 6 was synthesized according to a literature procedure.[91] The product was distilled under reduced pressure to give 5.2 g of the nitrate as a colorless oil (82%): ^{1}H NMR (CD_3CN) δ 5.49 (2 H, s), 7.44 (5 H, m); IR (neat) 1634, 1280 cm^{-1}.

2-Phenylcyclopropanecarboxaldehyde Oxime (11). To a solution of (2-phenylcyclopropyl)methanol (0.21 g, 1.4 mmol) in dry dichloromethane under nitrogen was added pyridinium chlorochromate (PCC) (0.34 g, 1.6 mmol). The mixture was allowed to stir overnight. The mixture was diluted with dichloromethane and then passed through a plug of Celite and silica gel. The solvent was removed to give 2-phenylcyclopropanecarboxaldehyde: ^{1}H NMR ($CDCl_3$) δ 1.5−1.8 (2 H, m), 2.17 (1 H, m), 2.65 (1 H, m), 7.07−7.38 (5 H, m), 9.32 (1 H, d, J = 5.2 Hz).

This aldehyde (0.21 g, 1.4 mmol) was dissolved in 4 mL of pyridine and hydroxylamine hydrochloride (0.11 g, 1.6 mmol) added. The mixture was allowed to stir for 1 h. Then the mixture was taken up in ethyl ether and washed with water, 10% aqueous hydrochloric acid (2×), and a saturated sodium bicarbonate solution. The organic layer was dried with magnesium sulfate, and the solvent was removed to give the oxime **11**: ^{1}H NMR ($CDCl_3$) δ 1.25−1.50 (2 H, m), 1.88 (1 H, m), 2.18 (1 H, m), 7.10−7.36 (6 H, m); IR (neat) 3307, 2923, 1651, 1456, 1261 cm^{-1}; MS (EI) m/z 161 (24), 144 (85), 115 (100); UV−vis (CH_3CN) λ_{max} 195, 225 nm (ϵ_{220} = 8615 M^{-1} cm^{-1}).[92]

4-Phenylbuten-4-one Oxime (12). To a solution of 4-phenylbuten-4-ol (0.50 g, 3.4 mmol) in dry dichloromethane under nitrogen was added PCC (0.80 g, 3.7 mmol). The mixture was allowed to stir overnight. The mixture was diluted with dichloromethane and then passed through a plug of Celite and silica gel. The solvent was removed to give 4-phenylbuten-4-one (0.36 g, 72%): ^{1}H NMR ($CDCl_3$) δ 3.76 (2 H, dt, J = 6.7 Hz, J = 1.4 Hz), 5.23 (2 H, m), 6.10 (1 H, m), 7.54 (3 H, m), 7.98 (2 H, m).

This ketone (0.36 g, 2.5 mmol) was dissolved in 2 mL of pyridine and hydroxylamine hydrochloride (0.19 g, 2.7 mmol) added. The mixture was allowed to stir for 1 h. The mixture was then taken up in ethyl ether and washed with water, 10% aqueous hydrochloric acid (2×), and a saturated sodium bicarbonate solution. The organic layer

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was dried with magnesium sulfate, and the solvent was removed to give the oxime **12**: ^{1}H NMR ($CDCl_3$) δ 3.59 (2 H, dt, J = 6.2 Hz, J = 1.7 Hz), 5.15 (2 H, m), 5.94 (1 H, m), 7.37 (3 H, m), 7.64 (2 H, m), 8.05 (1 H, br s); IR (neat) 3270 cm^{-1}; UV−vis (CH_3CN) λ_{max} 205, 248 nm (ϵ_{220} = 6140 M^{-1} cm^{-1}).[92]

Photolysis of Sulfoximines 1a−1c and 3. Irradiations were performed on solutions of reactant (10 or 1 mM) in acetonitrile or acetonitrile-d_3 in 1.0 cm quartz cuvettes, sealed with rubber septa, and purged with argon for 15 min prior to irradiation. Solutions were irradiated using a Rayonet reactor equipped with 254 nm low-pressure mercury arc lamps.

Photolysis of Phenanthrene-Releasing Precursors 2a−2c. Irradiations were performed on solutions of the reactant (1 mM) in acetonitrile or acetonitrile-d_3 in 16 mm Pyrex tubes, sealed with rubber septa, and purged with argon or oxygen for 15 min prior to irradiation. Solutions were irradiated using a Rayonet reactor equipped with 300 nm low-pressure mercury arc lamps.

Analysis of Reaction Mixtures. The products of the photolysis were preliminarily identified using GC/MS and then confirmed by NMR and HPLC with a co-injection of authentic material. Products were quantified by HPLC, GC, and NMR spectroscopy. For HPLC analyses a Waters C-18 Symmetry analytical column (3.9 × 150 mm), a Waters C-18 Symmetry analytical column (7.8 × 100 mm), or a Phenomenex C-18 Luna column (4.6 × 250 mm) was used with acetonitrile/water mixtures as eluents. The column used for GC analysis was an Alltech 30 m Econo-Cap EC-5 capillary column.

Trapping of Benzoxynitrene and Phenoxynitrene upon Photolysis of Phenanthrene-Releasing Precursors 2a and 2c in *cis*-2-Butene. In a typical experiment oxynitrene precursor 2a or 2c was placed in a Pyrex tube fitted with a dry ice condenser under nitrogen, and *cis*-2-butene was condensed into the tube to obtain a 1 mM solution. The solution was photolyzed with a Hanovia 450 W water-cooled medium-pressure mercury arc immersion lamp for 2 h. The reaction mixture was analyzed by GC/MS, NMR, and HPLC. The photolysis mixture was also compared with authentic aziridines using co-injection in HPLC. Comparison with authentic aziridines revealed that no trapping had occurred for benzoxynitrene and that phenoxynitrene was trapped with *cis*-2-butene to provide both the *cis*- and *trans*-*N*-phenoxy-2,3-dimethylaziridine, albeit in very low yield.

Trapping of the Oxynitrene Intermediate upon Photolysis of Phenanthrene-Releasing Precursors 2a and 2c by 1,4-Cyclohexadiene. A solution of oxynitrene precursor 2a or 2c (10 mM) in 1,4-cyclohexadiene was degassed and irradiated using a Rayonet reactor equipped with 350 nm low-pressure mercury arc lamps for 1 h. The reaction mixtures were analyzed by GC/MS, NMR, and HPLC. The photolysis mixtures were also compared with authentic *O*-hydroxylamines (free based from HCl salt with triethylamine) employing co-injections in HPLC. These analyses demonstrated that benzoxynitrene was not trapped, but phenoxynitrene was trapped to yield *O*-phenylhydroxylamine, the double H-atom abstraction product, in approximately 12% yield.

Time-Resolved IR Methods. The TRIR experiments have been conducted following the method of Hamaguchi and co-workers[93,94] as has been described previously.[95] Briefly, the broad-band output of a $MoSi_2$ IR source (JASCO) is crossed with excitation pulses from either a Quantronix Q-switched Nd:YAG laser (266 nm, 90 ns, 0.4 mJ) operating at 200 Hz or a Continuum Minilite II Nd:YAG laser (266 nm, 5 ns, 2 mJ) operating at 15 Hz. Changes in IR intensity are monitored using an ac-coupled mercury/cadmium/tellurium (MCT) photovoltaic IR detector (Kolmar Technologies, KMPV11-J1/AC), amplified, digitized with a Tektronix TDS520A oscilloscope, and collected on a Macintosh with IGOR for data processing. The experiment is conducted in dispersive mode with a JASCO TRIR 1000 spectrometer.

Electron Paramagnetic Resonance (EPR) Spectroscopy. A 20, 10, or 5 mM solution of the appropriate precursor in either methylcyclohexane or methylcyclopentane was subject to at least three freeze−pump−thaw cycles and sealed under vacuum in a 4 mm quartz EPR tube. The samples were placed in the cryostat at 10 K and photolyzed with an Oriel 250 W medium-pressure mercury arc lamp. The EPR spectra were obtained on an X-band Bruker EMX spectrometer with a gun diode as the microwave source running at 9.48 GHz. Samples were cooled by a continuous flow of helium using an Oxford ESR-900 cryostat with a model ITC 503 temperature controller. EPR spectra were recorded with a microwave power of 10 mW and modulation amplitude of 20 G with H_0 = 3382 G. Similar EPR spectra were obtained on an X-band Varian E12 spectrometer with a TE102 cavity and a klystron as a microwave source.

Computational Methods. Geometries were fully optimized at the respective level of theory, and all stationary points were confirmed to be energy minima by vibrational frequency analyses. The B3LYP,[96−98] MP2,[99] G2,[100] and CBS-QB3[101] calculations were performed with Gaussian 98[102] and provided the energy difference between the closed-shell singlet and the open-shell triplet states for the respective nitrenes. To compute the relative energy of the closed- and open-shell singlet states, MCSCF and MRCISD methods were employed with the MOLPRO program.[103] The active spaces for the MCSCF and subsequent MRCISD calculations were chosen such that, in the triplet state, one unoccupied orbital in each symmetry (a′ and a″ of C_s symmetry) at the Hartree−Fock configuration was included. For HO−N, CH_3O−N, and HS−N, an active space consisting of eight electrons distributed over seven molecular orbitals was used. For H_2N−N, an active space consisting of ten electrons distributed over nine molecular orbitals was used. Atomic spin densities, based on Löwdin charges, of triplet HO−N and CH_3O−N were calculated at the UMP2/6-311G**-optimized geometry using the UMP2/6-311G** wave functions.

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Supporting Information Available: Experimental details for the synthesis of authentic samples of *N*-phenoxy- and *N*-benzoxy-2,3-dimethylaziridines, computational results for heteroatomic nitrenes, and full references for Gaussian 98 and MOLPRO. This material is available free of charge via the Internet at http://pubs.acs.org.

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