O-Alkyl-*N*-acyl-*N*-phenylhydroxylamines as Photochemical Alkoxy Radical Precursors

Nilanjana Chowdhury, Anakuthil Anoop,* N. D. Pradeep Singh*

Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur 721302, India
Fax +91(3222)282252; E-mail: ndpradeep@chem.iitkgp.ernet.in

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Dedicated to Professor Eluvathongal D. Jemmis on the occasion of his 60th birthday

Abstract: A simple and efficient technique for the photolysis of alkoxy radical precursors is developed. Irradiation of *O*-alkyl-*N*-acyl-*N*-phenylhydroxylamines, as representative alkoxy radical precursors, with ultraviolet light (≥254 nm) results in homolytic N–O bond cleavage to generate singlet alkoxy and acylaminyl caged radical pairs. These radicals, depending on the solvent employed, either escape from the cage to form fragmentation products, or undergo in-cage reactions to produce photorearrangement products. The homolytic cleavage of the N–O bond is analyzed using time-dependent density functional theory calculations. The nature of the *N*-acyl substituent on the *O*-alkyl-*N*-acyl-*N*-phenylhydroxylamines is shown to influence their ability to generate radicals. Furthermore, identification and trapping of the alkoxy radicals is demonstrated.

Key words: alkoxy radicals, *O*-alkyl-*N*-acyl-*N*-phenylhydroxylamines, homolytic cleavage, acylaminyl radical, alkoxy radical precursors

Alkoxy radicals have been utilized for the synthesis of a wide variety of organic products,[1] and moreover, they are pivotal intermediates in several mechanistic[1b,e,2] and photobiological studies.[3] Alkoxy radicals primarily undergo three main reactions, namely β-cleavage,[4] 1,5-hydrogen atom transfer[5] and cyclization.[6] Several precursors for the generation of alkoxy radicals have been reported which include alkyl nitrites,[7] nitrates,[8] hypohalites,[9] sulfenyl ethers[10] and alkyl-4-nitrobenzenesulfenates.[11] However, these precursors often require acidic conditions, or reactive reagents to generate the alkoxy radicals, which may not be compatible with other labile functional groups present in the molecule. Hence, substrates which generate alkoxy radicals under photolytic or mild conditions (e.g., Bu_3SnH–AIBN) have become the subject of interest. Precursors such as *N*-alkoxy-pyridine-2-thiones,[2b] *Se*-phenyl benzoselenohydroximates,[12] *N*-alkoxyphthalimides,[13] *N*-alkoxy-2-pyridones,[14] and *N*-(alkoxy)thiazole-2(3*H*)-thiones[6c] have been used to generate alkoxy radicals efficiently via photoinduced homolytic cleavage of the weak N–O bond.

Significant progress has been made to understand the mechanism of N–O bond cleavage in *N*,*O*-diacyl-*N*-phenylhydroxylamines in connection with photoacyloxy rearrangement.[15] Sakurai and co-workers[15a] showed that *N*,*O*-diacyl-*N*-phenylhydroxylamines underwent efficient homolytic N–O bond cleavage on direct photolysis involving the singlet excited state, to form 1,3- and 1,5-acyloxy photorearrangement products along with fragmentation compounds (an arenecarboxanilide, a carboxylic acid and hydrocarbons). The products of photorearrangement were found to be derived from in-cage recombination of acyloxy and amido radicals, while formation of the fragmentation products was explained via a cage-escape mechanism of the above-mentioned radicals.[15,16] Interestingly, the same group showed that when the photolysis of *N*,*O*-diacyl-*N*-phenylhydroxylamines was carried out in hydrogen donor solvents, fragmentation products (carboxylic acid and carboxanilide) were produced exclusively, via efficient hydrogen atom abstraction from the solvent by cage-escaped acyloxy and amido radicals.[17] The above facts concerning the efficient photoinduced homolytic N–O bond cleavage chemistry of *N*,*O*-diacyl-*N*-phenylhydroxylamines, together with our interest in exploring the applications of those compounds,[18] prompted us to investigate the possibility of utilizing *O*-alkyl-*N*-acyl-*N*-phenylhydroxylamines as alkoxy radical precursors.

Herein, we report *O*-alkyl-*N*-acyl-*N*-phenylhydroxylamines as simple and efficient photochemical alkoxy radical precursors. The synthesis and characterization of the alkoxy radical precursors is discussed. We also studied in detail the photochemistry of *O*-alkyl-*N*-acyl-*N*-phenylhydroxylamines on alkoxy radical formation, the solvent effects on photoproduct distribution, analysis of N–O bond cleavage using theoretical calculations and the influence of *N*-acyl substituents on the ability to generate the alkoxy radical precursors. Furthermore, identification and trapping of the alkoxy radicals has been discussed.

O-Alkyl-*N*-benzoyl-*N*-phenylhydroxylamines **3a**–**m** were synthesized using the reported procedure[19] outlined in Scheme 1. Treatment of *N*-benzoyl-*N*-phenylhydroxylamine (**1**) with various alcohols **2a**–**m**, in the presence of diethyl azodicarboxylate (DEAD) and triphenylphosphine (Ph_3P) in tetrahydrofuran at room temperature for a period of 18 hours, afforded the corresponding alkoxy radical precursors **3a**–**m**[20] in good to excellent yields (cf. Table 3). The precursors **3a**–**m** were characterized by ^1H, ^{13}C NMR and IR spectroscopy and mass spectrometry.

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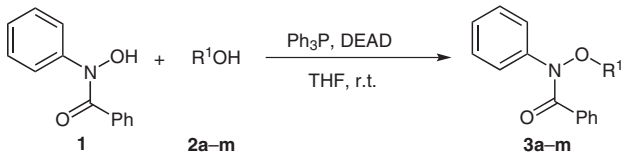


R^1 = benzyl (**3a**), phenylethyl (**3b**), phenylpropyl (**3c**), 3,4-dimethoxy phenylpropyl (**3d**), cinnamyl (**3e**), phenylbutyl (**3f**), decyl (**3g**), tetradecyl (**3h**), tetrahydrofuran-2-methyl (**3i**), pent-4-enyl (**3j**), 2-phenylpent-4-enyl (**3k**), 5-phenylpent-4-enyl (**3l**) 4-phenylpent-4-enyl (**3m**)

Scheme 1 Synthesis of *O*-alkyl-*N*-benzoyl-*N*-phenylhydroxylamines **3a**–**m**

Initially, we investigated the photolysis of *O*-benzyl-*N*-benzoyl-*N*-phenylhydroxylamine (**3a**) (0.2 mM) in an oxygen-free acetonitrile solution using a medium pressure mercury lamp (125 W) with a quartz sleeve. Similar to *N*,*O*-diacyl-*N*-phenylhydroxylamines,[15] alkoxy radical precursor **3a** underwent photoinduced homolytic N–O bond cleavage to generate singlet benzyloxy and benzanilidyl radical cage pairs (Scheme 2). These radicals escape from the cage to produce the fragmentation products, benzyl alcohol (**2a**), benzanilide (**4**) and benzaldehyde (**5**). Interestingly, we also found that an in-cage reaction of the above-mentioned radical pairs occurred to yield photorearrangement products **6a** and **6b**. Compound **6a** was identified by isolation and comparison with an authentic sample. Since 1,3-photorearrangement product **6b** was only formed in a small amount, it was not isolated, but instead was identified from the crude NMR spectra of the photolysate by comparison with that of a known sample.[21]

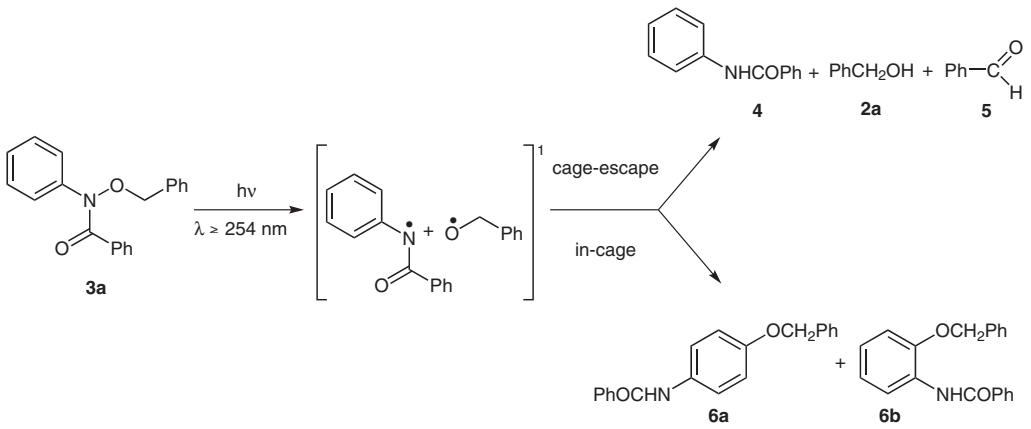
To study the effect of solvents on the formation of the photoproducts and their distribution, we carried out the photolysis of **3a** (0.2 mM) in hydrogen atom free solvents [benzene, trifluorotoluene ($PhCF_3$), dichloroethane (DCE)], poor hydrogen atom donor solvents (acetonitrile, aqueous methanol), and an efficient hydrogen atom donor solvent (anhydrous benzene containing Bu_3SnH) over three hours (Table 1). We observed that alkoxy radical precursor **3a** produced low yields of fragmentation products **2a** and **4** in benzene and trifluorotoluene. In these solvents, competing pathways such as α-hydrogen abstraction from the benzyloxy radical by the benzanilidyl radical to form benzaldehyde (**5**), and minor processes resulting in dimerization, disproportionation and addition reactions of benzanilidyl radicals are favored.[22] However, in solvents with an abstractable hydrogen atom (aqueous methanol and acetonitrile), we noted higher yields of benzyl alcohol (**2a**) and benzanilide (**4**). More interestingly, in anhydrous benzene containing four equivalents of tributyltin hydride (Bu_3SnH), we observed the formation of benzyl alcohol and benzanilide, exclusively, from alkoxy radical precursor **3a**. As a representative example, we have included the HPLC traces recorded at regular intervals during the photolysis of **3a** on irradiation in aqueous methanol (see Supporting Information, Figure 1s). This solvent study indicated that the photolysis of **3a** proceeded via homolysis of the N–O bond.

Table 1 Distribution of the Photoproducts of *O*-Benzyl-*N*-benzoyl-*N*-phenylhydroxylamine (**3a**) in Various Solvents

Solvent	Unreacted **3a** (%)[a]	Yield of photoproducts (%)[a]			
		4	**2a**	**5**	**6a**
C_6H_6	25	25	26	8	12
$PhCF_3$	20	28	32	5	10
DCE	20	30	35	<2	8
MeCN	18	32	38	–	5
aq MeOH	15	35	42	–	–
C_6H_6[b]	5	42	48	–	–

[a] Yield calculated from NMR spectra using anisole as an internal standard.
[b] Containing Bu_3SnH (4 equiv).

We have also performed time-dependent density functional theory (TDDFT) calculations (see computational methods for details), on alkoxy radical precursor **3a** in order to analyze the N–O bond cleavage mechanism. The four lowest vertical excitation energies at the TD-B3LYP/def2-SVP level of theory and their oscillator strengths are given in Table 2.



Scheme 2 Photolysis of *O*-benzyl-*N*-benzoyl-*N*-phenylhydroxylamine (**3a**) in acetonitrile

Table 2 Low-Lying Excited States, Excitation Energies and Oscillator Strengths of *O*-Benzyl-*N*-benzoyl-*N*-phenylhydroxylamine (**3a**) Obtained from TD-B3LYP/def2-SVP Calculations

State	Excitation energy (eV)	Oscillation strength
S1	4.16	0.106114620990912100
S2	4.43	0.007424637903512666
S3	4.71	0.012829276438581270
S4	4.77	0.011781504286684200

The ground state potential energy surface (PES) for N–O bond cleavage was analyzed by a relaxed surface scan (Figure 1) with fixed N–O distances, from 1.364–2.263 Å in 0.1 Å steps. All coordinates, except the N–O bond distance were allowed to be optimized. The BP86/def2-SVP method was used for this scan. The energy was found to increase with increasing N–O bond distance, and the system eventually dissociates into two fragments. The bond dissociation energy (BDE) for the homolytic cleavage from the ground state minima was 48.21 kcal/mol and the process was endothermic. The potential energy surface (TD-BP86/def2-SVP) for the first singlet excited surface (S1) was analyzed using a similar surface scan to that described above. The estimated activation barrier was 11.35 kcal/mol. A similar value (12 kcal/mol) was found for *N*-(trifluoromethanesulfonyloxy)-1,8-naphthalimide using the estimated barrier from the surface scan of the single point S1 state energies at ground state (S0) geometries.[23] In contrast, the N–O bond dissociation in alkyl nitrites was barrierless.[24] The geometry at the highest point was further optimized using the dimer method which allowed the transition state to be located. The transition state was characterized using vibrational frequency analysis. The activation barrier including zero-point correction was 10.56 kcal/mol. Minima and transition state geometries at the S1 surfaces were also computed using the B3LYP functional and def2-SVP basis set; the activation barrier was found to be 10.64 kcal/mol. All the above computations were performed using the restricted Kohn–Sham formalism. When unrestricted formalism was employed, a lower barrier of 6.1 kcal/mol was obtained. Since unrestricted calculations are more reliable for homolysis reactions, the 6.1 kcal/mol value should be considered as a more accurate barrier for the N–O bond cleavage. The bond dissociation energy determined from the excited state minima (S1) was –2.75 kcal/mol and the bond cleavage was exothermic. Heterolytic cleavage, leading to dissociation into cationic and anionic fragments, can be ruled out as it is an endothermic (by 198.11 kcal/mol) process.

To demonstrate the applicability of alkoxy radical precursors for the generation of various alcohols, we irradiated solutions of *O*-alkyl-*N*-benzoyl-*N*-phenylhydroxylamines **3a**–**m** (0.2 mM) in anhydrous benzene (containing 4 equiv of Bu_3SnH) using a medium pressure mercury lamp with a quartz sleeve for two to five hours. The corresponding free alcohols **2a**–**m** were obtained in high yields (85–95%) as shown in Table 3. In each case the photoproducts were isolated and analyzed by NMR spectroscopy (data were compared with those of authentic samples). We found that the free alcohols were the major photoproducts in addition to benzanilide (**4**). The quantum yields for the generation of the alcohols were found to be in the range 0.008–0.015% using valerophenone as an actinometer.[25]

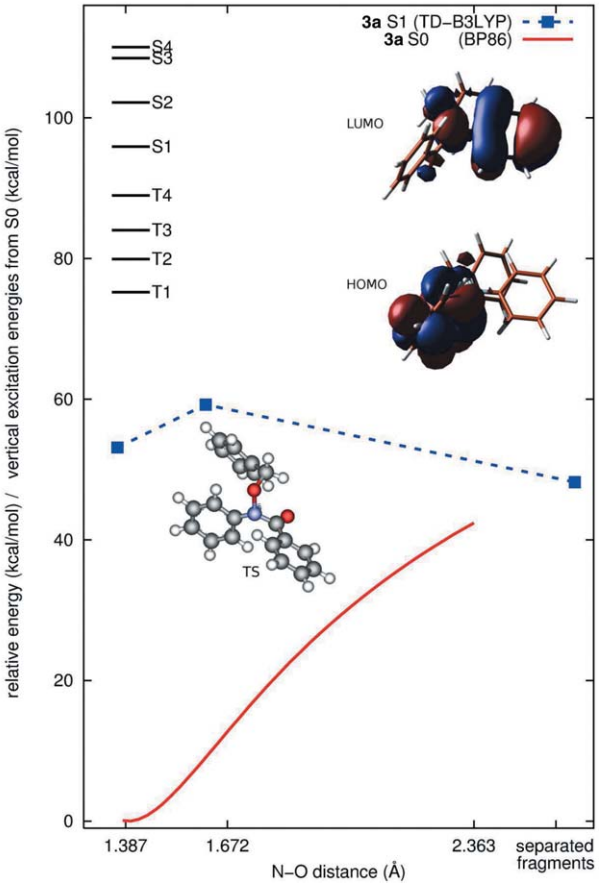


Figure 1 Potential energy surface for the thermal dissociation (red solid curve; BP86/def2-SVP) and the reaction profile for the photochemical dissociation (blue dashed line; TD-UB3LYP/def2-SVP) of N–O bonds. The geometry of the transition state and the HOMO and LUMO orbitals are also shown.

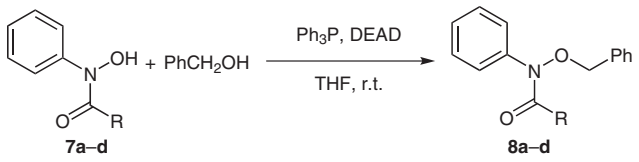
To demonstrate the requirement of ultraviolet light for the generation of alkoxy radicals, we carried out control experiments, which involved maintaining a solution of the alkoxy radical precursor **3a**–**m** in anhydrous benzene (containing 4 equiv of Bu_3SnH) in the dark for a period of 15 days. HPLC analysis showed that under these conditions the alkoxy radical precursors were stable and that no photoproducts were produced. In addition, we verified the propensity for alkoxy radical generation from *O*-alkyl-*N*-benzoyl-*N*-phenylhydroxylamines under standard radical conditions, by treating **3a** with tributyltin hydride (1.2 equiv) and 2,2′-azobis(isobutyronitrile) (AIBN) as the initiator in benzene at reflux temperature for five hours, which resulted in formation of benzyl alcohol (**2a**) in a good 70% yield.

Table 3 Synthetic Yield, UV/Vis and Photolysis Data of *O*-Alkyl-*N*-benzoyl-*N*-phenylhydroxylamines **3a**–**m**

Radical precursor	Yield (%)[a]	UV/Vis λ (nm)[b]	log ε[c]	Time (h)[d]	Alcohol	Photolysis yield (%)[e]	Quantum yield (%)[f]
3a	95	258	4.16	3.0	**2a**	95	0.015
3b	92	259	4.16	3.0	**2b**	90	0.014
3c	85	260	4.14	3.0	**2c**	88	0.013
3d	89	278	4.25	3.5	**2d**	92	0.012
3e	85	261	4.20	2.5	**2e**	90	0.018
3f	80	260	4.18	3.5	**2f**	89	0.009
3g	87	258	4.03	4.5	**2g**	87	0.008
3h	87	258	4.02	4.8	**2h**	85	0.013
3i	90	259	4.08	3.0	**2i**	85	0.008
3j	82	257	4.09	5.0	**2j**	85	0.009
3k	87	260	4.17	4.8	**2k**	88	0.009
3l	92	261	4.18	5.0	**2l**	90	0.008
3m	90	261	4.18	4.5	**2m**	85	0.008

[a] Yield of isolated products **3**.
[b] Maximum absorption wavelength (λ_{max}).
[c] Molar absorption coefficient.
[d] Time required for photolysis.
[e] Photolysis yield of **2** based on ^{1}H NMR spectroscopy.
[f] Quantum yield for the alcohols at room temperature (error limit within ±5%).

We next investigated the effect of various *N*-acyl substituents on the alkoxy radical precursors on their ability to generate radicals. Thus, *O*-benzyl-*N*-acyl-*N*-phenylhydroxylamines **8a**–**d** were prepared from substrates **7a**–**d** (Scheme 3).



R = Me (**8a**), 4-$O_2NC_6H_4$ (**8b**), 3,4-$(MeO)_2C_6H_3$ (**8c**), 4-ClC_6H_4 (**8d**)

Scheme 3 Synthesis of *O*-benzyl-*N*-acyl-*N*-phenylhydroxylamines **8a**–**d**

To compare the efficiency of different *N*-acyl derivatives of *O*-benzyl-*N*-phenylhydroxylamines for the generation of benzyloxy radicals, we irradiated compounds **3a** and **8a**–**d** in anhydrous benzene (containing 4 equiv of Bu_3SnH) for three hours using a light source of ≥254 nm, and monitored the formation of benzyl alcohol by HPLC at regular time intervals. From the HPLC data, the natural logarithm of the concentration of benzyl alcohol formed (lnC) versus irradiation time (t) was plotted for each alkoxy radical precursor. We observed linear correlations for the formation of benzyl alcohol which suggested a first order reaction, obtained by linear least-square methodology for a straight line (see Supporting Information, Figure 2s). Further, we also calculated the first order photolysis rate constant (K) values from the slope [lnC versus irradiation time (t)] for the formation of benzyl alcohol from the alkoxy radical precursors. The quantum yield (Φ) and photolysis rate constant values (Table 4) indicate that the *N*-acyl substituents influence the formation of benzyl alcohol. We found that alkoxy radical precursor **8c**, possessing an electron-donating 3,4-dimethoxybenzoyl substituent, showed the lowest quantum yield for the formation of benzyl alcohol among the precursors investigated. The above effect can be due to destabilization of the newly generated acylaminyl radical by the strongly electron-donating acyl substituents.[26] Hence, the present study indicates that the *N*-acyl substituents influence the ability of the substrates to generate radicals.

We were also interested in demonstrating these *O*-alkyl-*N*-acyl-*N*-phenylhydroxylamines as synthetic precursors for the stereoselective synthesis of tetrahydrofurans, as has been previously reported in the literature.[6] Photolysis of compounds **3j**–**l** in the presence of four equivalents of tributyltin hydride in trifluorotoluene for three hours resulted in formation of substituted tetrahydrofurans **10j**–**l** (Scheme 4). Among the precursors, photolysis of **3l** produced 2-benzyltetrahydrofuran (**10l**, 75%, Table 5, entry 2),[27] along with benzanilide (**4**, 85%), aldehyde **9l** (5%)

Table 4 Synthetic Yield, UV/Vis and Photolysis Data of *O*-Benzyl-*N*-acyl-*N*-phenylhydroxylamines **3a** and **8a–d**

Radical precursor	Yield (%)[a]	λ_{max} (nm)[b]	log ε[c]	K (min^{-1})[d]	Photolysis yield (%)[e]	Quantum yield (%)[f]
3a	92	258	4.16	2.00×10^{-2}	95	0.015
8a	90	247	4.06	1.90×10^{-2}	92	0.015
8b	90	278	4.02	1.37×10^{-2}	90	0.014
8c	88	290	4.14	0.33×10^{-2}	88	0.006
8d	85	264	4.49	1.40×10^{-2}	90	0.013

[a] Yield of isolated product.
[b] Maximum absorption wavelength.
[c] Molar absorption coefficient.
[d] Rate constant.
[e] Photolysis yield of benzyl alcohol based on ^{1}H NMR spectroscopy of the crude reaction mixture using anisole as an internal standard.
[f] Quantum yield for the formation of benzyl alcohol at room temperature (error limit within ±5%).

and alkenol **2l** (4%). The formation of 2-benzyltetrahydrofuran can be explained via 5-*exo* ring-closure of the alkoxy radical intermediate. In contrast, photolysis of compound **3l** in benzene in the presence of tributyltin hydride produced 2-benzyltetrahydrofuran in 65% yield (Table 5, entry 1). Irradiation of **3k** in trifluorotoluene (containing 4 equiv of Bu_3SnH) resulted in formation of the substituted tetrahydrofuran **10k** in 64% yield (Table 5, entry 5), whereas compound **3j**, under similar conditions, produced a 30% yield of unsubstituted tetrahydrofuran (Table 5, entry 3).

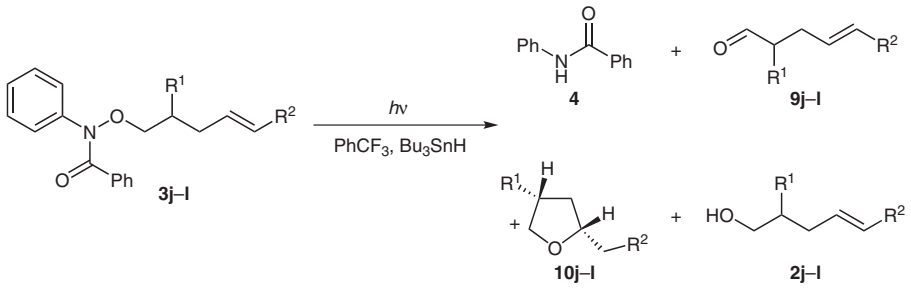
The possibility of heteroatom-trapping under photolytic conditions was explored using bromotrichloromethane

Table 5 Synthesis of Tetrahydrofurans **10j–l**

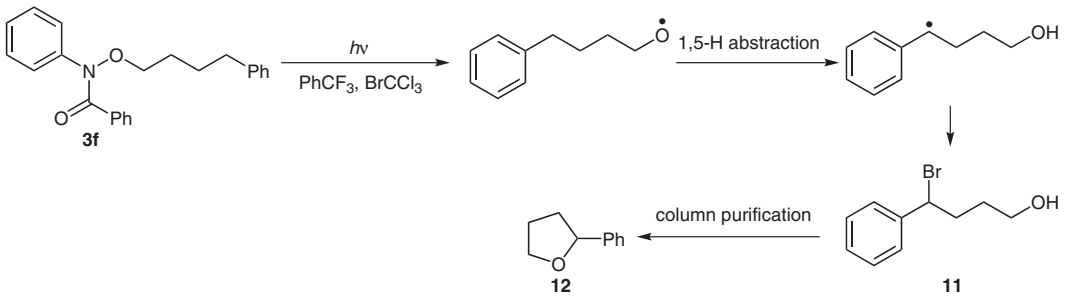
Entry	Substrate	R^1	R^2	Solvent[a]	Product	Yield (*cis*/*trans*)
1	**3l**	H	Ph	C_6H_6	**10l**	65[b]
2	**3l**	H	Ph	$PhCF_3$	**10l**	75 [72][b]
3	**3j**	H	H	$PhCF_3$	**10j**	30[b]
4	**3k**	Ph	H	C_6H_6	**10k**	59 (80/20)[b]
5	**3k**	Ph	H	$PhCF_3$	**10k**	64 (80/20)[b]
6[c]	**3l**	H	Ph	C_6H_6	**10l**	–

[a] In each case, the solvent contained Bu_3SnH (4 equiv).
[b] Yield calculated by NMR spectroscopy of the crude reaction mixture using anisole as an internal standard. Yield of isolated product is provided in square brackets.
[c] No product was obtained in the absence of light.

($BrCCl_3$) as a bromine atom donor and alkoxy radical precursor **3f** as the *O*-radical source. Photolysis of compound **3f** and bromotrichloromethane in trifluorotoluene using a medium pressure mercury lamp (125 W) produced a 37% yield of 4-bromo-4-phenylbutanol (**11**);[6b,c,28] the yield was calculated by ^{1}H NMR spectroscopy of the crude reaction mixture using anisole as an internal standard. The formation of compound **11** can be explained via 1,5-hydrogen transfer from carbon to the oxygen-centered radical followed by bromine atom abstraction by the newly generated carbon-centered radical (Scheme 5). Further, compound **11** cyclized into 2-phenyltetrahydrofuran (**12**)[29] on purification by silica gel column chromatography.



Scheme 4 Synthesis of tetrahydrofurans **10j–l** from *O*-alkyl-*N*-acyl-*N*-phenylhydroxylamines **3j–l**



Scheme 5 Trapping of a carbon-centered radical using bromotrichloromethane ($BrCCl_3$)

In summary, we have reported *O*-alkyl-*N*-acyl-*N*-phenylhydroxylamines as efficient alkoxy radical precursors based on photoinduced N–O bond cleavage chemistry. Formation of the photoproducts and their distribution in different solvents along with time-dependent density functional theory calculations indicated that photolysis of the alkoxy radical precursors proceeded through homolysis of the N–O bond from the singlet excited state. Interestingly, the ability of *O*-alkyl-*N*-acyl-*N*-phenylhydroxylamines to generate alkoxy radicals was shown to be altered by different *N*-acyl substituents. Further, we demonstrated the identification and trapping of the newly generated alkoxy radicals via intramolecular addition to double bonds and homolytic substitution.

Reactions were monitored using precoated silica gel 60 F254 TLC sheets (Merck). Chromatographic purification was performed using 60–120 mesh silica gel (Merck). Petroleum ether (PE) refers to the fraction boiling in the 40–60 °C range. Melting points were obtained using a REICO apparatus and are uncorrected. FT-IR spectra were obtained using a Perkin Elmer RXI spectrometer. ^{1}H NMR (200 MHz) spectra were recorded on a Bruker-AC 200 MHz spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), integration. ^{13}C NMR (50 MHz) spectra (proton decoupled) were recorded on a Bruker-AC 200 MHz spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm). UV/Vis absorption spectra were recorded on a Shimadzu UV-2450 UV/Vis spectrophotometer. High-resolution mass spectra were obtained using an LCT Micromass spectrometer. HPLC was performed using a Shimadzu Prominence (LC 20 AT) liquid chromatography instrument on a C_{18} column (4.5 mm × 250 mm) with a UV/Vis detector. Photolysis of all compounds was carried out using a 125 W medium pressure mercury lamp supplied by SAIC (India).

Computational Methods

Density functional theory (DFT) calculations were performed using the BP86[30] and B3LYP[31] functionals with empirical dispersion correction (DFT-D)[32] in conjunction with the def2-SVP[33] basis set. Resolution of the identity (RI) approximation was used to speed-up the BP86 calculations. TURBOMOLE V6.2[34] was used for all calculations. For excited state calculations, time-dependent density functional theory (TDDFT) was employed. We included the four lowest roots for each calculation. Dl-find,[35] implemented in ChemShell[36] was used for optimizations. The dimer method[37] was employed in order to compute transition states at the excited state potential energy surface (PES). Vibrational analysis for excited states was performed using finite-difference Hessian evaluation implemented in ChemShell, and for ground state structures, analytic gradients from TURBOMOLE V6.2 were used.

_O_-Alkyl-_N_-benzoyl-_N_-phenylhydroxylamines 3a–m; General Procedure

To a soln of *N*-benzoyl-*N*-phenylhydroxylamine (**1**) (789 mg, 3.70 mmol), alcohol **2** (3.08 mmol) and Ph_3P (1.2 g, 4.6 mmol) in THF (10 mL) was added DEAD (0.73 mL, 4.6 mmol) in THF (10 mL) at r.t. under an N_2 atm. After stirring for 18 h at r.t., the mixture was diluted with H_2O (5 mL) and extracted with EtOAc (50 mL). The combined organic layer was dried over anhyd $MgSO_4$, filtered, concentrated and purified.

_O_-Benzyl-_N_-benzoyl-_N_-phenylhydroxylamine (3a)

The crude residue was purified by column chromatography (EtOAc–hexane, 9:41) to give the title compound.

Yield: 1.00 g (95%); white solid; mp 85–87 °C.

IR (KBr): 1648 (C=O) cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.87 (s, 2 H), 7.17 (d, *J* = 4.0 Hz, 2 H), 7.24–7.47 (m, 9 H), 7.56 (d, *J* = 8.0 Hz, 2 H), 7.65 (d, *J* = 6.6 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 73.9, 124.2 (2 C), 126.9, 127.9 (2 C), 128.5 (2 C), 128.6 (2 C), 128.9, 129.0 (2 C), 129.7 (2 C), 130.6, 134.1, 134.9, 139.7, 168.6.

HRMS (ES+): *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{17}NO_2Na$: 326.1157; found: 326.1129.

_O_-Phenylethyl-_N_-benzoyl-_N_-phenylhydroxylamine (3b)

The crude residue was purified by column chromatography (EtOAc–hexane, 1:5) to give the title compound.

Yield: 1.08 g (92%); brown solid; mp 90–92 °C.

IR (KBr): 1645 (C=O) cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.86 (t, *J* = 6.8 Hz, 2 H), 4.12 (t, *J* = 6.8 Hz, 2 H), 7.09–7.13 (m, 2 H, ArH), 7.18–7.46 (m, 11 H), 7.65 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 34.5, 74.8, 123.9 (2 C), 126.6, 126.8, 128.0 (3 C), 128.5 (4 C), 128.9 (3 C), 130.7, 134.7, 137.5, 139.7, 168.3.

HRMS (ES+): *m*/*z* $[M + H]^+$ calcd for $C_{21}H_{20}NO_2$: 318.1494; found: 318.1425.

_O_-Phenylpropyl-_N_-benzoyl-_N_-phenylhydroxylamine (3c)

The crude residue was purified by column chromatography (EtOAc–hexane, 1:5) to give the title compound.

Yield: 1.08 g (85%); brown liquid.

IR (neat): 1645 (C=O) cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.77–1.90 (m, 2 H), 2.54 (t, *J* = 7.4 Hz, 2 H), 3.88 (t, *J* = 6.2 Hz, 2 H), 7.02 (d, *J* = 7.4 Hz, 2 H), 7.16–7.27 (m, 4 H), 7.30–7.50 (m, 7 H), 7.63 (d, *J* = 6.4 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.6, 31.9, 73.6, 124.3 (2 C), 126.0, 127.0, 128.0 (2 C), 128.4 (4 C), 128.6 (2 C), 129.0 (2 C), 130.6, 134.8, 139.8, 141.2, 168.2.

HRMS (ES+): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{22}NO_2$: 332.1650; found: 332.1603.

_O_-(3,4-Dimethoxyphenylpropyl)-_N_-benzoyl-_N_-phenylhydroxylamine (3d)

The crude residue was purified by column chromatography (EtOAc–hexane, 1:4) to give the title compound.

Yield: 1.20 g (89%); yellow liquid.

IR (neat): 1647 (C=O) cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.79–1.86 (m, 2 H), 2.50 (t, *J* = 8.0 Hz, 2 H), 3.83 (s, 6 H), 3.90 (t, *J* = 6.2 Hz, 2 H), 6.54–6.60 (m, 2 H), 6.73 (d, *J* = 8.0 Hz, 1 H), 7.24–7.39 (m, 6 H), 7.47 (d, *J* = 8.8 Hz, 2 H), 7.62 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.8, 31.6, 55.8, 55.9, 73.6, 111.3, 111.7, 120.2, 124.3 (2 C), 127.0, 127.9 (2 C), 128.5 (2 C), 128.9 (2 C), 130.5, 133.9, 134.8, 139.8, 147.3, 148.9, 168.2.

HRMS (ES+): *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{26}NO_4$: 392.1862; found: 392.1894.

_O_-Cinnamyl-_N_-benzoyl-_N_-phenylhydroxylamine (3e)

The crude residue was purified by column chromatography (EtOAc–hexane, 1:4) to give the title compound.

Yield: 1.05 g (89%); brown liquid.

IR (neat): 1648 (C=O) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 4.53 (d, *J* = 7.0 Hz, 2 H), 6.07–6.18 (m, 1 H), 6.52 (d, *J* = 16.0 Hz, 1 H), 7.21–7.46 (m, 11 H), 7.55 (d, *J* = 8.2 Hz, 2 H), 7.66 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 75.0, 122.3, 124.5 (2 C), 126.8 (2 C), 127.0, 128.0 (2 C), 128.4, 128.6 (2 C), 128.7 (2 C), 129.0 (2 C), 130.7, 134.9, 136.0, 136.4, 139.9, 168.4.

HRMS (ES+): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{20}NO_2$: 330.1494; found: 330.1478.

O-Phenylbutyl-*N*-benzoyl-*N*-phenylhydroxylamine (3f)
The crude residue was purified by column chromatography (EtOAc–hexane, 9:41) to give the title compound.

Yield: 1.02 g (80%); yellow liquid.

IR (neat): 1642 (C=O) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.43–1.46 (m, 4 H), 2.47–2.60 (m, 2 H), 3.88 (s, 2 H), 7.09 (d, *J* = 7.6 Hz, 2 H), 7.18 (t, *J* = 7.2 Hz, 1 H), 7.24–7.29 (m, 3 H), 7.33–7.42 (m, 5 H), 7.50 (d, *J* = 7.6 Hz, 2 H), 7.63 (d, *J* = 7.2 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.4 (2 C), 35.4, 74.1, 123.9 (2 C), 125.8, 126.8, 127.9 (2 C), 128.3 (2 C), 128.4 (2 C), 128.5 (2 C), 129.0 (2 C), 130.5, 134.9, 139.8, 141.9, 168.4.

HRMS (ES+): *m*/*z* $[M + H]^+$ calcd for $C_{23}H_{24}NO_2$: 346.1807; found: 346.1797.

O-Decyl-*N*-benzoyl-*N*-phenylhydroxylamine (3g)
The crude residue was purified by column chromatography (EtOAc–hexane, 3:17) to give the title compound.

Yield: 1.10 g (87%); brown liquid.

IR (neat): 1640 (C=O) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 5.4 Hz, 3 H), 1.16–1.24 (m, 14 H), 1.38–1.48 (m, 2 H), 3.83 (t, *J* = 6.4 Hz, 2 H), 7.17–7.29 (m, 1 H), 7.34–7.39 (m, 5 H), 7.53 (d, *J* = 8.0 Hz, 2 H), 7.65 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.3, 22.9, 25.9, 28.0, 29.4, 29.5, 29.6 (2 C), 32.1, 74.6, 123.8 (2 C), 126.8, 128.0 (2 C), 128.6 (2 C), 129.0 (2 C), 130.6, 135.1, 139.9, 168.5.

HRMS (ES+): *m*/*z* $[M + H]^+$ calcd for $C_{23}H_{32}NO_2$: 354.2433; found: 354.2481.

O-Tetradecyl-*N*-benzoyl-*N*-phenylhydroxylamine (3h)
The crude residue was purified by column chromatography (EtOAc–hexane, 3:17) to give the title compound.

Yield: 1.22 g (87%); brown liquid.

IR (neat): 1640 (C=O) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.0 Hz, 3 H), 1.14–1.26 (m, 20 H), 1.30–1.38 (m, 2 H), 1.39–1.47 (m, 2 H), 3.81 (t, *J* = 6.4 Hz, 2 H), 7.19 (t, *J* = 7.2 Hz, 1 H), 7.33–7.39 (m, 5 H), 7.52 (d, *J* = 7.6 Hz, 2 H), 7.63 (d, *J* = 6.8 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1, 22.7, 25.7, 27.9, 29.2, 29.4, 29.5, 29.6 (5 C), 31.9, 74.4, 123.6 (2 C), 126.6, 127.8 (2 C), 128.4 (2 C), 128.8 (2 C), 130.5, 134.9, 139.7, 168.3.

HRMS (ES+): *m*/*z* $[M + H]^+$ calcd for $C_{27}H_{40}NO_2$: 410.3059; found: 410.3025.

O-[(Tetrahydrofuran-2-yl)methyl]-*N*-benzoyl-*N*-phenylhydroxylamine (3i)
The crude residue was purified by column chromatography (EtOAc–hexane, 3:22) to give the title compound.

Yield: 0.99 g (90%); brown liquid.

IR (neat): 1638 (C=O) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.30–1.34 (m, 1 H), 1.41–1.53 (m, 1 H), 1.70–1.89 (m, 2 H), 3.63–3.69 (m, 2 H), 3.73–3.88 (m, 2 H), 3.92–4.08 (m, 1 H), 7.16–7.27 (m, 1 H), 7.29–7.42 (m, 5 H), 7.46 (d, *J* = 9.6 Hz, 2 H), 7.52–7.59 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.5, 28.0, 63.8, 75.8, 76.5, 123.9 (2 C), 126.8, 127.9 (2 C), 128.5 (2 C), 128.9 (2 C), 130.6, 134.7, 139.6, 168.3.

HRMS (ES+): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{20}NO_3$: 298.1443; found: 298.1454.

O-(Pent-4-enyl)-*N*-benzoyl-*N*-phenylhydroxylamine (3j)
The crude residue was purified by column chromatography (EtOAc–hexane, 3:22) to give the title compound.

Yield: 0.95 g (82%); brown liquid.

IR (neat): 1640 (C=O) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.48–1.67 (m, 2 H), 1.92–2.02 (m, 2 H), 3.86 (t, *J* = 6.4 Hz, 2 H), 4.84–4.92 (m, 2 H), 5.56–5.76 (m, 1 H), 7.13–7.25 (m, 1 H), 7.33–7.42 (m, 5 H), 7.49 (d, *J* = 7.6 Hz, 2 H), 7.63 (d, *J* = 6.2 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 36.6, 44.3, 77.6, 116.7, 123.8, 126.7, 127.8 (2 C), 127.9 (2 C), 128.4 (2 C), 128.8 (2 C), 130.5, 135.6, 140.9, 168.2.

HRMS (ES+): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{20}NO_2$: 282.1494; found:282.1428.

O-(2-Phenylpent-4-enyl)-*N*-benzoyl-*N*-phenylhydroxylamine (3k)
The crude residue was purified by column chromatography (EtOAc–hexane, 3:17) to give the title compound.

Yield: 0.92 g (87%); brown liquid.

IR (neat): 1642 (C=O) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.18–2.43 (m, 2 H), 2.79–2.93 (m, 1 H), 4.03–4.08 (m, 2 H), 4.88 (d, *J* = 13.8 Hz, 2 H), 5.44–5.60 (m, 1 H), 7.05–7.77 (m, 15 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 36.7, 44.3, 76.6, 116.7, 123.8, 126.7, 127.8 (2 C), 127.9 (3 C), 128.5 (4 C), 128.8 (3 C), 130.5, 134.7, 135.6, 139.4, 141.0, 168.2.

HRMS (ES+): *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{24}NO_2$: 358.1807; found: 358.1834.

O-(5-Phenylpent-4-enyl)-*N*-benzoyl-*N*-phenylhydroxylamine (3l)
The crude residue was purified by column chromatography (EtOAc–hexane, 3:17) to give the title compound.

Yield: 1.21 g (92%); brown liquid.

IR (neat): 1641 (C=O) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.68–1.81 (m, 2 H), 2.15–2.25 (m, 2 H), 3.97 (t, *J* = 6.2 Hz, 2 H), 6.01–6.16 (m, 1 H), 6.30 (d, *J* = 16.0 Hz, 1 H), 7.12–7.50 (m, 11 H), 7.58 (d, *J* = 7.8 Hz, 2 H), 7.72 (d, *J* = 7.8 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.7, 29.2, 73.6, 124.1 (2 C), 126.0 (2 C), 126.9, 127.1, 128.0 (2 C), 128.6 (4 C), 129.0 (2 C), 129.3, 130.7, 130.8, 134.9, 137.6, 139.8, 168.4.

HRMS (ES+): *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{24}NO_2$: 358.1807; found: 358.1836.

O-(4-Phenylpent-4-enyl)-*N*-benzoyl-*N*-phenylhydroxylamine (3m)
The crude residue was purified by column chromatography (EtOAc–hexane, 3:17) to give the title compound.

Yield: 1.24 g (92%); brown liquid.

IR (neat): 1641 (C=O) cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.64–1.71 (m, 2 H), 2.47 (t, *J* = 7.2 Hz, 2 H), 3.93 (t, *J* = 6.2 Hz, 2 H), 4.97 (s, 1 H), 5.29 (s, 1 H), 7.20–7.41 (m, 11 H), 7.61 (d, *J* = 8.0 Hz, 2 H), 7.72 (d, *J* = 7.8 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.4, 31.4, 73.8, 112.7, 123.8 (2 C), 126.1 (2 C), 126.8, 127.6, 128.0 (2 C), 128.4 (2 C), 128.5 (2 C), 129.0 (2 C), 130.6, 135.1, 139.9, 140.8, 147.3, 168.4.

HRMS (ES+): *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{24}NO_2$: 358.1807; found: 358.1824.

***N*-[4-(Benzyloxy)phenyl]benzamide (6a)**

An oxygen-free soln of **3a** (100 mg, 0.33 mmol) in MeCN (30 mL) was irradiated with a 125 W medium pressure Hg lamp filtered by a quartz glass for 3 h. The extent of reaction was monitored by TLC at regular intervals. After complete consumption of the starting material as indicated by TLC, the solvent was removed under vacuum and the photoproducts were isolated by column chromatography (see below). The structures of the isolated photoproducts, benzanilide (**4**) (55 mg, 85%), benzyl alcohol (**2a**) (27 mg, 75%) and **6a** (3 mg, 4%) were confirmed by NMR spectroscopy and by comparison with authentic samples. The other photoproducts, benzaldehyde (**5**) and 1,3-alkoxy photorearrangement product **6b** were characterized by NMR spectroscopy of the crude reaction mixture using anisole as an internal standard. The title compound **6a** was obtained following purification of the crude residue by column chromatography (EtOAc–hexane, 7:13).

Yield: 3 mg (4%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.07 (s, 2 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 7.33–7.55 (m, 10 H), 7.69 (br s, 1 H), 7.86 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 70.2, 115.3 (2 C), 121.9, 125.1, 126.9 (2 C), 127.4 (2 C), 127.9, 128.5 (2 C), 128.6, 128.7 (2 C), 131.1, 131.7, 136.8, 155.8, 165.7.

Photolysis of *O*-Benzyl-*N*-benzoyl-*N*-phenylhydroxylamine (3a); Solvent Effect

Photolysis of **3a** (100 mg, 0.33 mmol) was carried out in 25 mL each of anhyd benzene, $PhCF_3$, MeCN, aq MeOH and Bu_3SnH (4 equiv) in benzene for 3 h. The solvent was removed under vacuum and the yields of the photoproducts in the crude reaction mixture determined by NMR spectroscopy using anisole as an internal standard.

Photogeneration of Alcohols from *O*-Alkyl-*N*-benzoyl-*N*-phenylhydroxylamines 3 and Quantum Yield Measurements

A soln of compound **3a**–**m** (100 mg, 0.33 mmol) in anhyd benzene (30 mL) containing Bu_3SnH (0.8 mmol) was irradiated with a 125 W medium pressure Hg lamp filtered by a quartz glass. The extent of reaction was monitored at regular intervals by HPLC (hexane–*i*PrOH, 9:1), at a flow rate of 1 ml/min (UV detection at 254 nm). After completion of the reaction, the solvent was removed under vacuum and the major photoproducts, benzanilide (**4**) and alcohols **2a**–**m** were isolated by column chromatography (PE–EtOAc, 7:1) and then analyzed by NMR spectroscopy.

The quantum yields of the alcohols were analyzed by ^{1}H NMR spectroscopy employing valerophenone as an actinometer. The percentage of alcohol generated was determined by calculating the gradual increase in the peak area of the alcohol using anisole as an internal standard.

***O*-Benzyl-*N*-acyl-*N*-phenylhydroxylamines 8a–d; General Procedure**

To a soln of *N*-acyl-*N*-phenylhydroxylamine **7** (3.30 mmol), benzyl alcohol (**2a**) (0.3 g, 3.08 mmol) and Ph_3P (1.2 g, 4.6 mmol) in THF (10 mL) was added DEAD (4.6 mmol) in THF (10 mL) at room temperature under an N_2 atm. After stirring for 18 h at r.t., the mixture was diluted with H_2O (5 mL) and extracted with EtOAc (50 mL). The combined organic layer was dried over anhyd $MgSO_4$, filtered, concentrated and purified.

***O*-Benzyl-*N*-acetyl-*N*-phenylhydroxylamine (8a)**

The crude residue was purified by column chromatography (EtOAc–hexane, 1:5) to give the title compound.

Yield: 0.73 g (92%); yellow liquid.

IR (neat): 1660 (C=O) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.19 (s, 3 H), 4.82 (s, 2 H), 7.26 (t, *J* = 7.2 Hz, 1 H), 7.34–7.44 (m, 7 H), 7.55 (d, *J* = 7.2 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.9, 76.2, 128.4 (3 C), 128.7 (3 C), 128.9, 129.5 (3 C), 134.2, 138.6, 170.2.

HRMS (ES+): *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{16}NO_2$: 242.1181; found: 242.1103.

***O*-Benzyl-*N*-(4-nitrobenzoyl)-*N*-phenylhydroxylamine (8b)**

The crude residue was purified by column chromatography (EtOAc–hexane, 3:7) to give the title compound.

Yield: 0.63 g (90%); white solid; mp 112–115 °C.

IR (KBr): 1653 (C=O) cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.78 (s, 2 H), 7.04 (d, *J* = 7.0 Hz, 2 H), 7.23–7.37 (m, 4 H), 7.45 (t, *J* = 8.0 Hz, 2 H), 7.57 (d, *J* = 7.4 Hz, 2 H), 7.67 (d, *J* = 8.2 Hz, 2 H), 8.17 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 76.5, 123.0 (2 C), 124.1, 127.6, 128.6 (2 C), 129.2 (2 C), 129.3 (2 C), 129.5 (2 C), 129.7 (2 C), 133.5, 138.5, 140.8, 148.6, 166.4.

HRMS (ES+): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{17}N_2O_4$: 349.1188; found: 349.1116.

***O*-Benzyl-*N*-(3,4-dimethoxybenzoyl)-*N*-phenylhydroxylamine (8c)**

The crude residue was purified by column chromatography (EtOAc–hexane, 3:7) to give the title compound.

Yield: 0.57 g (88%); yellow liquid.

IR (neat): 1648 (C=O) cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.75 (s, 3 H), 3.87 (s, 3 H), 4.87 (s, 2 H), 6.77 (d, *J* = 8.4 Hz, 1 H), 7.17–7.46 (m, 12 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.8, 55.9, 76.5, 110.1, 112.3, 122.9, 124.5 (2 C), 126.6, 126.9, 128.4 (2 C), 128.8, 129.0 (2 C), 129.6 (2 C), 134.4, 140.4, 148.2, 151.2, 167.7.

HRMS (ES+): *m*/*z* calcd for $C_{22}H_{22}NO_4$: 364.1549; found: 364.1532.

***O*-Benzyl-*N*-(4-chlorobenzoyl)-*N*-phenylhydroxylamine (8d)**

The crude residue was purified by column chromatography (EtOAc–hexane, 1:4) to give the title compound.

Yield: 0.62 g (90%); yellow liquid.

IR (neat): 1652 (C=O) cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.81 (s, 2 H), 7.11–7.16 (m, 2 H), 7.24–7.44 (m, 8 H), 7.53 (t, *J* = 6.0 Hz, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 76.5, 124.2 (2 C), 127.2, 128.2 (2 C), 128.6 (2 C), 129.0, 129.1 (2 C), 129.7 (2 C), 130.3 (2 C), 133.1, 133.9, 136.7, 139.4, 167.4.

HRMS (ES+): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{17}ClNO_2$: 338.0948; found: 338.0988.

Photolysis of Compounds 3a and 8a–d

A soln of compound **3a** or **8a**–**d** (100 mg, 0.33 mmol) in anhyd benzene (30 mL) containing Bu_3SnH (4 equiv) was irradiated using a 125 W medium pressure Hg lamp filtered by a quartz glass. The extent of reaction was monitored at regular intervals by HPLC (hexane–*i*-PrOH, 9:1), at a flow rate of 1 ml/min (UV detection at 254 nm) . The HPLC data was used to plot the logarithm of concentration of benzyl alcohol generated (lnC) versus the irradiation time (*t*) for each alkoxy radical precursor.

2-Benzyltetrahydrofuran (10l);[27] Typical Procedure
In a quartz glass test-tube, *O*-(5-phenyl-4-pentenyl)-*N*-benzoyl-*N*-phenylhydroxylamine (**3l**) (100 mg, 0.28 mmol) was dissolved in $PhCF_3$ (50 mL). Bu_3SnH (0.25 mL, 1.1 mmol) was added and the mixture degassed under an N_2 atm for 20 min. The soln was irradiated using a 125 W medium pressure Hg lamp filtered by a quartz glass for 3 h. After completion of the reaction, the solvent was evaporated under reduced pressure and the residue purified by column chromatography (PE–Et_2O, 2:1) to afford 2-benzyltetrahydrofuran (**10l**).

Yield: 30 mg (72%); colorless liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.55–1.60 (m, 1 H), 1.83–1.97 (m, 3 H), 2.69–2.79 (m, 1 H), 2.88–2.98 (m, 1 H), 3.68–3.79 (m, 1 H), 3.84–3.91 (m, 1 H), 3.98–4.10 (m, 1 H), 7.16–7.36 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.7, 31.1, 42.0, 67.9, 80.1, 126.2, 128.3 (2 C), 129.3 (2 C), 139.0.

The same procedure described above was employed for the photolysis of compounds **3j** and **3k** and the resulting cyclized tetrahydrofurans were characterized by NMR spectroscopy of the crude photoproducts.

2-Phenyltetrahydrofuran (12);[29] Carbon-Centered Radical Trapping
In a quartz glass test tube, *O*-(4-phenylbutyl)-*N*-benzoyl-*N*-phenylhydroxylamine (**3f**) (75 mg, 0.21 mmol) was dissolved in $PhCF_3$ (15 mL). $BrCCl_3$ (0.06 mL, 0.63 mmol) was added and the mixture degassed under an N_2 atm for 20 min. The soln was irradiated using a 125 W medium pressure Hg lamp filtered by a quartz glass for 6 h. After completion of the reaction, the solvent was evaporated under reduced pressure and the residue purified by column chromatography to furnish 4-phenyl-4-bromobutanol (**11**) (characterized from the crude ^{1}H NMR spectrum) and 2-phenyltetrahydrofuran (**12**).

Yield: 4 mg (25%); colorless liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.83–2.00 (m, 1 H), 2.03–2.18 (m, 2 H), 2.31–2.34 (m, 1 H), 3.85–3.92 (m, 2 H), 4.82 (t, *J* = 6.6 Hz, 1 H), 7.40–7.60 (m, 5 H).

Generation of Alkoxy Radicals from Compound 3a under Standard Radical Conditions
A soln of compound **3a** (100 mg, 0.33 mmol) in anhyd benzene (15 mL) containing Bu_3SnH (0.11 mL, 1.2 equiv) and AIBN (0.03 equiv) was heated at 80 °C for 5 h. The solvent was evaporated and the crude residue purified by column chromatography (EtOAc–hexane, 3:17) to afford benzyl alcohol (**2a**) (24 mg, 70%) and benzanilide (**4**) (51 mg, 80%).

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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