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Solid state generation of phenoxyl radicals through β-fragmentation from specifically designed diazenes. An ESR investigation

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ABSTRACT

Upon irradiation at room temperature, symmetrical diazene precursors enabled the formation of phenoxyl radicals through β-fragmentation reaction in the solid state. This traceless generation of phenoxyl radicals was investigated by ESR. This study showed that although the fragmentation of β-phenoxy radicals is a slow process in solution, it could be useful in solid state thanks to the absence of faster competitive pathways.

1. Introduction

Phenoxyl radicals are a very interesting class of radicals. They are involved in a broad spectrum of domains ranging from chemical biology[1] or metal complexes[2] to materials chemistry[3] with applications in radical batteries[4] or in organic magnetism.[5] Most phenoxyl radicals are transient as illustrated by their extinction rate constants.[6] Their lifetime increases when *ortho* and *para* bulky substituents are present, which decreases their reactivity by hindering the carbon atoms bearing the highest spin densities.[7] From a synthetic point of view, phenoxyl radicals are mainly involved in dimerization or polymerization processes.[8]

In previous studies, we have shown that the lifetime of a transient radical, like aryl sulfanyl radicals, can be dramatically increased when their precursors either form an organic monolayer in the pore[9] of a nanostructured silica or are anchored in its framework.[10] We wanted to extend this concept to a more challenging radical: the phenoxyl radical. Indeed, unlike phenyl sulfanyl radical in which the spin density is centered on the sulfur atom, the spin density in phenoxyl radical is largely delocalized on the carbon atoms of the aromatic ring which results in an increase of the number of propagation and termination reactions. To trigger the generation of a radical in a nanostructured organic-inorganic hybrid silica a clean method was needed in order to avoid the formation of other paramagnetic species and thus to facilitate the study of the radical functionalized material.

Many methodologies lead to the formation of phenoxyl radicals.[11] They can be generated by oxidation of the corresponding phenols with metal salts ($K_3Fe(CN)_6$,[12] $FeCl_3$,[13] $Ce(SO_4)_2$,[14] $Pb(OAc)_4$[15]), metal oxides (PbO_2,[16] Ag_2O,[17] MnO_2[18]), organic oxidizing agent like quinones,[19] enzymatic systems,[20] dioxygen under basic conditions[21] and by electrochemistry.[4,22] Hydrogen atom abstraction by another radical,[11b] typically an alkoxyl radical, has also been described.[23] Conversely, they can also be formed from 4-halo-2,5-cyclohexadienones by using reductive metals (Hg, Ag, Cu, Zn, Na, K).[24] All these methods need a solvent and produce by-products incompatible with the purpose of our study.

Photochemistry might offer an alternative. The homolysis of ArO-H or ArO-Alkyl bonds at 254 nm leads to phenoxyl radicals but with low photochemical yields.[25] Moreover, the energetic wavelength needed to promote these cleavages might be the source of other undesired homolysis. The photolytic rearrangement of an aromatic nitro group at 330–380 nm is a milder way to produce a phenoxyl radical[26] but the concomitant generation of a persistent radical, i.e., nitrogen monoxide, precludes its use for the present study.

For the traceless generation of arylsulfanyl radicals in the framework of hybrid silicas, we have designed diazene based precursors which release the sulfur centered radicals via the β-fragmentation of an appropriately designed tertiary carbon-centered radical formed by the decomposition of a diazene moiety upon irradiation at 360 nm (Scheme 1).[10]

We guessed that a similar strategy could be applied to the generation of phenoxyl radicals. The β-fragmentation of β-oxygen carbon-centered radicals is not a common route to release oxygen-centered radicals, yet, a few exceptions have been reported in the

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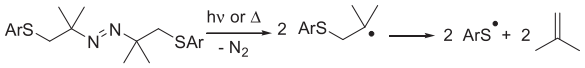


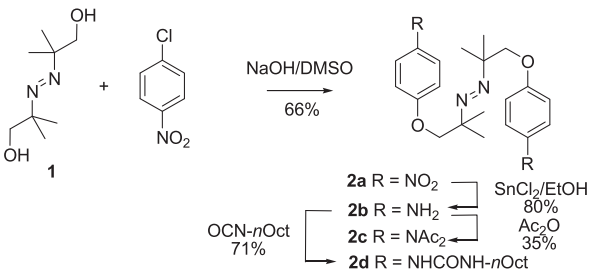
Scheme 1. Arylsulfanyl radical generation through double fragmentation.

literature such as the ring opening of vinyl epoxides[27] or the use of fluoropyridoxyl radical as leaving group in the allylic alcohols based radical allylation reactions recently devised by Zard.[28] The design of the latter originates from the observation of the unanticipated fragmentation of β-*p*-chlorophenoxyl radicals thanks to the reversible radical trapping in xanthate chemistry.[29] The fragmentation of β-oxygen carbon-centered radicals is also implied in the Surzur-Teissier reaction and related rearrangements.[30]

Herein, we report the behavior of diazene based precursors for the generation of phenoxyl radicals in solution and in solid phase as a study preliminary to the design of ordered silicas grafted with the same radical precursors.

2. Results and discussion

The skeleton of the diazene precursors was readily prepared by nucleophilic substitution of *p*-chloronitrobenzene with diol **1** (Scheme 2). The *p*-nitro precursor **2a** was subsequently reduced into the corresponding *p*-amino diazene **2b**, which in turn was converted into the corresponding bis-acetylamino and ureido derivatives **2c** and **2d**.



Scheme 2. Synthesis of diazene based precursors **2a**–**d**.

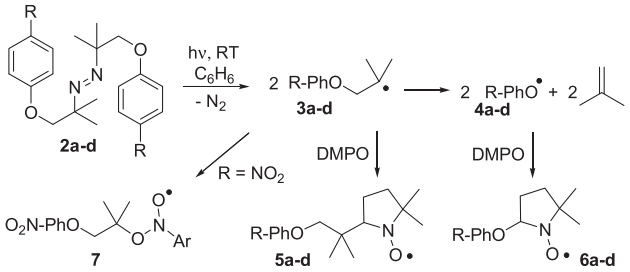
The nitro group was converted into different amino-(**2b**), imido-(**2c**) or urea-groups (**2d**) in order to mimic the linker devised to anchor the diazene precursor to nanostructured silicas, in view of the upcoming study of the impact of the structure of hybrid materials on the release and the persistence of phenoxyl radicals.

The fragmentation of diazenes **2a**–**d** was studied at room temperature by ESR under different conditions, in solution (spin trapping experiments) and in solid-state.

2.1. ESR fragmentation studies in solution

In a typical procedure, a solution of substrate (**2a**–**d**) and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO, 0.1 or 2 equiv) was degassed (10^{-5} mbar) in a 4 mm quartz-glass tube and radicals were generated via the light-induced decomposition of the diazene inside the spectrometer cavity (xenon lamp (200–800 nm) fitted with a 360±10 nm filter). The experiments were performed in benzene with the exception of **2d** for which toluene was used for the sake of solubility.

The 360 nm irradiation of diazene **2a**–**d** enables the formation of tertiary carbon centered radicals **3a**–**d**.[31] In the presence of a spin trap agent, these intermediates can evolve through two main pathways (Scheme 3):



Scheme 3. Photolysis of diazene precursors in the presence of DMPO.

- Addition to DMPO that produces adducts **5a**–**d**.
- β-Fragmentation that releases phenoxyl radicals **4a**–**d** and subsequently gives rise to adducts **6a**–**d**.

Whatever the amount of DMPO, in all cases, the irradiation enabled the characterization of spin adduct **5**.

The hyperfine coupling constants of nitroxydes **5a**–**d** reported Table 1 are in good agreement with the trapping of tertiary carbon centered radicals, likely to be **3a**–**d** (Fig. 1).[32] In the case of **2a**, a competitive trapping by the nitro group is likely to explain the presence of **7**.[33]

Table 1
ESR splitting constant of **5a**–**d**, **6a**–**d** and **7**

	DMPO	**5a**–**d**[b]		**6a**–**d**[b]				**7**
		a_N	a_H	a_N	a_H	a_H	a_H	a_N
2a	0.1 equiv	14.2	21.9	—	—	—	—	14.8
2a	2 equiv	14.2	21.9	—	—	—	—	—
2b	0.1 equiv	14.3	22.0	—	—	—	—	—
2b	2 equiv	14.2	22.0	—	—	—	—	—
2c	0.1 equiv	14.2	22.1	12.6	8.1	—	—	—
2c	2 equiv	14.2	22.1	—	—	—		—
2d[a]	0.1 equiv	—	—	12.9[c]	6.9	1.7	0.8	—
2d[a]	2 equiv	14.2	21.8	—	—	—	—	—

[a] In toluene.
[b] Hyperfine splitting constants (G) of adduct.
[c] After turning off the irradiation.

The lowering of DMPO concentration allowed radical **3** to evolve via fragmentation. Consequently, the adduct of phenoxyl radical[6] was only detected with **2c** in the presence of 10% of DMPO.[34] The behavior of **2d** was slightly different. A complex signal was recorded with a small amount of spin trap. After turning off the irradiation, a simplification of the signal enabled the observation of **6d**.

It can be underlined that when the same experiments were performed without spin trap, a complex ESR signal was recorded for substrate **2b**–**d**. This complexity was not unexpected considering the fast rate of polymerization of phenoxyl radicals.[6] In the case of **2a**, only the characteristic triplet signal of an *N*-alkyloxy *N*-aryl nitroxide of type **7** (g=2.0058), resulting from the addition of the tertiary carbon centered radical **3a** to the nitro group, was detected.[33] In other words, the nitro group acted as spin trap agent.

These experiments showed that a fast trapping of **3** occurred. In only two cases, the formation of phenoxyl radicals was evidenced by spin adducts **6c** and **6d**. This observation performed in the presence of 10% of DMPO confirmed the low rate of the β-fragmentation of radicals **3** in solution. This is in agreement with the fragmentation rate estimated by Zard with a cyclobutylcarbinyl radical probe for the release of fluoropyridoxyl radical (i.e., 10^3–10^4 s^{-1}).[28a]

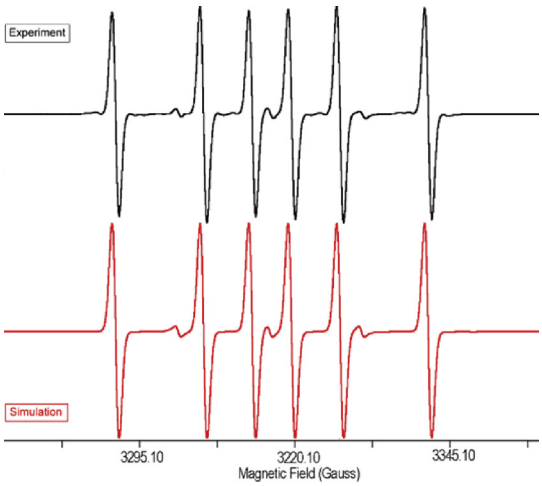


Fig. 1. ESR spectrum of **5c** at room temperature (irradiation of **2c** in the presence of DMPO (2 equiv)), the small triplet (a_N=14.8 G) fits DMPO degradation by product.[32]

2.2. ESR studies at solid state

Radical precursors **2** were designed to generate phenoxyl radicals grafted to nanostructured silica in the solid state. Prior to this study, in order to investigate the behavior of **2** under close conditions, ESR experiments were directly performed on the solid precursors at room temperature.

The powders (**2a**–**d**) were degassed (10^{-5} mbar) in a 4 mm quartz-glass tube and irradiated at 293 K with a xenon lamp (200–800 nm) fitted with a 360 nm filter.

In the absence of solvent, the direct ESR observation of the fragmentation of diazene precursor **2a**–**d** showed the formation of phenoxyl radicals **4a**–**d**. An anisotropic signal was recorded for all precursors (Fig. 2) but **2d**, for which an isotropic signal was observed.

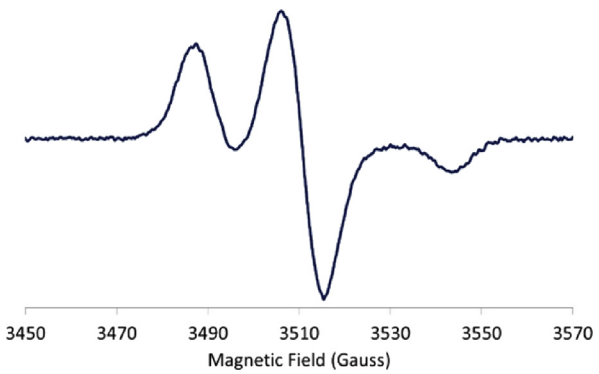


Fig. 2. ESR. Spectrum of **4b** powder at room temperature.

The ESR parameters of these signals were in agreement with the formation of phenoxyl radicals.[21b,35] *g* Factors are gathered in Table 2. It must be outlined that the solid state generation has a dramatic impact on the half-lives of these phenoxyl species. The decay curves were fitted with exponential or multi-exponential models, which did not allow to determine the mechanism involved. The half-lifetimes were graphically estimated from the decay curves. Half-lives ranging from 11 min to higher than 8 days were registered. This is likely to correlate to the solid state and the restricted mobility which, in anaerobic medium, should slow down most decay pathways via dimerization.

Table 2
g Tensors for **4a**–**d**

	g_z	g_y	g_x	g_{iso}[a]	$t_{1/2}$
4a	1.990	2.005	2.018	2.004	5.9 h
4b	1.990	2.005	2.019	2.005	—[b]
4c	1.990	2.005	2.018	2.004	11 min
4d	—	—	—	2.004	>8 j

[a] $g_{iso}=(g_x+g_y+g_z)/3$.
[b] Not determined.

In the case of radical **4b**, an intense ESR signal was recorded prior to irradiation. The increase of the signal was weak under irradiation as well as its decrease after the end of the photolysis. This phenomenon might be due to the interference of spontaneous or photo-stimulated electron transfer reactions.

Under these conditions the tertiary carbon centered radicals **3a**–**d** were not observed. Unlike the ESR experiment performed in solution, only the phenoxyl radicals were detected. Although slow, the fragmentation of the β-oxygen carbon-centered radicals occurred cleanly. The fact that the experiments were achieved under vacuum does not seem to favour the fragmentation since the same results were observed under argon.

3. Conclusion

This ESR study showed that diazene-based precursors do not enable an efficient generation of phenoxyl radicals in solution. However, the low rate of the β-fragmentation step does not impede the generation of phenoxyl radical in the solid state to be observed. No faster competitive pathway occurs thanks to the absence of diffusion.

This type of precursor is a candidate of choice to generate phenoxyl radicals from hybrid materials since it is stable under the conditions necessary to the silica synthesis. No co-reagent is needed and consequently no solvent is required. The side products (nitrogen and isobutene) resulting from the fragmentation diffuse readily in the silica matrix[10] and thus no other radical species is generated.

It is reasonable to assume that this approach to produce aryl-heteroatomic radicals will apply to heteroatoms other than oxygen since the cleavage of the C–O bond is thermodynamically among the most unfavorable fragmentation processes.

4. Experimental section

4.1. General information

All reactions were carried out in dry glassware using magnetic stirring and a positive pressure of argon. Solvents are commercially available, they were used as purchased without further purification. THF was distilled over sodium benzophenone ketyl prior to use. Anhydrous DMSO was purchased. Dry state adsorption conditions and purification were performed on Macherey Nagel silica gel 60 A (70–230 mesh). Analytical thin layer chromatography was performed on pre-coated silica gel plates. Visualization was accomplished by UV (254 nm), with *p*-anisaldehyde and with phosphomolybdic acid in ethanol. ^{1}H NMR, ^{13}C NMR spectra were recorded on 300 or 400 MHz spectrometer. Chemical shifts (δ) are reported in ppm. Signals due to residual protonated solvent (^{1}H NMR) or to the solvent (^{13}C NMR) served as the internal standard: $CDCl_3$ (7.27 ppm and 77.0 ppm), DMSO-d_6 (2.50 ppm and 39.52 ppm). Multiplicity is indicated by one or more of the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), br (broad). The lists of coupling constants (J) reported in Hertz (Hz) correspond to the order of multiplicity

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assignment. APT was used for ^{13}C spectra assignment. All melting points were uncorrected and were recorded in open capillary tubes using a melting point apparatus. EPR experiments were performed with commercially available HPLC grade solvents and reactants that were used as received. EPR experiments were performed on an ELEXSYS Bruker instrument and the Bruker BVT 3000 set-up was utilized to control the temperature. Irradiations were performed with a Hamamatsu LC8 01A light source with a 360–370 nm filter. EPR spectra were simulated using WinSim 2002 software.

Diol **1** was prepared according to a literature procedure.[10]

4.2. Synthesis of compounds 2a–d

*4.2.1. (E)-1,2-Bis(2-methyl-1-(4-nitrophenoxy)propan-2-yl)diazene (**2a**).* To a solution of **1** (217 mg, 1.25 mmol, 1 equiv) and *p*-nitrochlorobenzene (432 mg, 2.74 mmol, 2.2 equiv) in DMSO (2 mL) under argon was slowly added NaOH (175 mg, 4.36 mmol, 3.5 equiv) at 0 °C. The mixture was stirred one night at room temperature. After completion (TLC monitoring, pentane/EtOAc: 80/20), the mixture was diluted with water and extracted three times with CH_2Cl_2. Organic phase was washed with water and brine, dried over $MgSO_4$ and concentrated. The residue was taken on Et_2O, stirred for 1 night, and filtrated to give **2a** as a white crystal (345 mg, 0.83 mmol, 66%). Mp 148–149 °C. ^1H NMR (400 MHz, $CDCl_3$) δ: 8.16 (d, J=9.3, 4H, ArH), 6.90 (d, J=9.3, 4H, ArH), 4.19 (s, 4H, CH_2), 1.27 (s, 12H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.3 (C_{ar}–O), 141.7 (C_{ar}–N), 126.0 (HC_{ar}), 114.7 (HC_{ar}), 74.5 (CH_2), 69.5 (C–N), 22.2 (CH_3). HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{20}H_{24}N_4O_6$: 417.1769 Da, found: 417.1768 Da.

*4.2.2. (E)-4,4′-((Diazene-1,2-diylbis(2-methylpropane-2,1-diyl))bis(oxy))dianiline (**2b**).* To a solution of **2a** (47 mg, 0.11 mmol, 1 equiv) in EtOH (1.5 mL) was added $SnCl_2{\cdot}2H_2O$ (248 mg, 1.1 mmol, 10 equiv). The resulting mixture was stirred one night at 60 °C. After completion (TLC monitoring, pentane/EtOAc: 50/50), the mixture was diluted with iced water and a solution saturated of $NaHCO_3$ was added until pH=7–8. The mixture was extracted three times with EtOAc, washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified using silica gel column (30–50% EtOAc in pentane) to give **2b** as a red solid (32 mg, 0.09 mmol, 80%). Mp 98–99 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 6.72 (d, J=8.4, 4H, ArH), 6.61 (d, J=8.4, 4H, ArH), 3.99 (s, 4H, CH_2), 1.23 (s, 12H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 143.43 (C_{ar}–O), 140.0 (C_{ar}–N), 116.5 (HC_{ar}), 116.2 (HC_{ar}), 76.7 (CH_2), 69.6 (C–N), 22.2 (CH_3). HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{20}H_{29}N_4O_2^+$: 357.2285 Da, found: 357.2284 Da.

*4.2.3. (E)-N,N′-(((Diazene-1,2-diylbis(2-methylpropane-2,1-diyl))bis(oxy))bis(4,1-phenylene))bis(N-acetylacetamide) (**2c**).* To a flask containing **2b** (100 mg, 0.28 mmol, 1 equiv) under argon was added acetic anhydride (0.92 mL, 9.52 mmol, 34 equiv). The mixture was stirred 5 days at 60 °C. After completion (NMR monitoring), the mixture was diluted with water and extracted three time with CH_2Cl_2. Organic phase was washed with $NaHCO_3$, brine, dried over $MgSO_4$ and concentrated. The residue was purified using silica gel column (40–60% AcOEt in pentane) to give **2c** as a yellow solid (51 mg, 0.097 mmol, 35%). Mp 92–94 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.01 (d, J=9.0 Hz, 4H, ArH), 6.93 (d, J=9.0 Hz, 4H, ArH), 4.11 (s, 4H, CH_2), 2.27 (s, 12H, $COCH_3$), 1.26 (s, 12H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.5 (CO), 159.4 (C_{ar}–O), 132.1 (C_{ar}–N), 129.7 (HC_{ar}), 115.8 (HC_{ar}), 74.4 (CH_2), 69.4 (C–N), 27.1 ($COCH_3$), 22.2 (CH_3). HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{28}H_{37}N_4O_6^+$: 525.2708 Da, found: 525.2707 Da.

*4.2.4. (E)-1,1′-(((Diazene-1,2-diylbis(2-methylpropane-2,1-diyl))bis(oxy))bis(4,1-phenylene))bis(3-octylurea) (**2d**).* To a solution of **2b** (200 mg, 0.56 mmol, 1 equiv) in THF (3.5 mL) was added octyl isocyanate (0.22 mL, 1.23 mmol, 2.2 equiv). The mixture was stirred one night at room temperature. After completion (TLC monitoring, pentane/EtOAc: 50/50), the mixture was diluted with Et_2O. The residue was filtrated, washed with Et_2O and dried to give a pale rose solid (267 mg, 0.40 mmol, 71%). Mp 172–173 °C. ^1H NMR (400 MHz, DMSO-d_6) δ: 8.15 (br s, 2H, NH), 7.23 (d, J=8.8 Hz, 4H, ArH), 6.75 (d, J=9.0 Hz, 4H, ArH), 5.97 (t, J=5.5 Hz, 2H, NH), 4.04 (s, 4H, O–CH_2), 3.03 (pseudo q, J=6.4 Hz, 4H, $NHCH_2$), 1.38 (t, J=6.2 Hz, 4H, CH_2CH_3), 1.26 (br s, 20H, CH_2), 1.16 (s, 12H, C_{quat}–CH_3), 0.86 (t, J=6.2 Hz, 6H, CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$+TFA d_1) δ: 158.2 (HNCONH), 129.0 (HC_{ar}), 127.5 (C_{ar}), 116.6 (HC_{ar}), 78.0 (CH_2–O), 71.8 (C_{quat}–N), 42.8 ($HNCH_2$), 32.2 (CH_2), 30.2 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 27.0 (CH_2), 23.0 (CH_2), 21.3 (CH_3–C_{quat}), 13.6 (CH_3). HRMS (ESI): m/z: calcd for $[M+H]^+$ $C_{38}H_{63}N_6O_4^+$: 667.4905, found: 667.4903.

4.3. ESR experiments

4.3.1. Spin-trapping experiments. In a 4 mm quartz-glass tube, 4 mg of diazene precursor and DMPO (2 or 0.1 equiv) in 0.25 mL of benzene were degassed with three freeze-pump-thaw cycles with a 10^{-5} mbar vacuum pump. EPR spectra were recorded at room temperature with the parameters: modulation amplitude=0.5 G, receiver gain=99 dB, modulation frequency=100 kHz, power=2 mW (20 dB), sweep width=100 G, conversion time=29.30 ms, sweep time=30 s, number of scans=1.

4.3.2. Solid state ESR experiments – direct observation. In solution: in a 4 mm quartz-glass tube, 5 mg of diazene precursor in 0.25 mL of benzene were degassed with three freeze-pump-thaw cycles with a 10^{-5} mbar vacuum pump. EPR spectra were recorded at room temperature with the parameters: modulation amplitude=0.5 G, receiver gain=99 dB, modulation frequency=100 kHz, power=2 mW (20 dB), sweep width=100 G, conversion time=29.30 ms, sweep time=30 s, number of scans=1.

Solid state: in a 4 mm quartz-glass tube, 5 mg of diazene precursor were degassed with three freeze-pump-thaw cycles with a 10^{-5} mbar vacuum pump. EPR spectra were recorded with the parameters: modulation amplitude=2 G, receiver gain=99 dB, modulation frequency=100 kHz, power=0.2 mW (30 dB), sweep width=200 G, conversion time=29.30 ms, sweep time=30 s, number of scans=2.

The half-lifetimes were estimated after turning off the irradiation by monitoring the decay of the signal intensity (determined from the double integrated EPR signal). The decay curves were fitted with exponential or multi-exponential models, which did not allow the mechanism involved to be determined. Several termination processes occurred. The half-lifetimes were graphically estimated from the decay curves.

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