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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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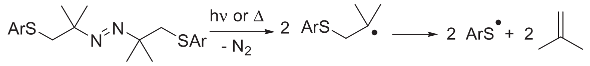


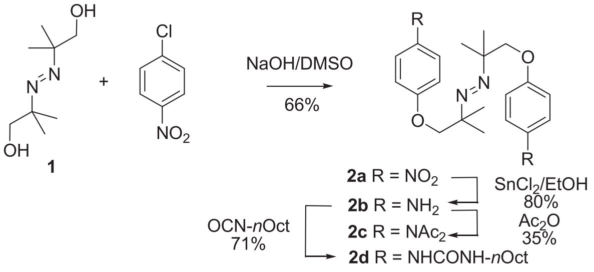
Scheme 1. Arylsulfanyl radical generation through double fragmentation.

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.

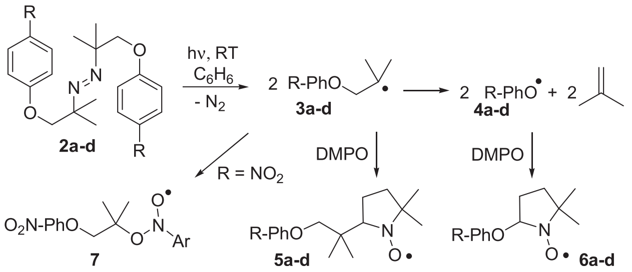
The fragmentation of diazenes **2a**–**d** was studied at room temperature by ESR under different conditions, in solution (spin trapping experiments) and in solid-state.

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):

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



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

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]