Tetrahedron Letters 59 (2018) 3124–3127

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Stability of twisted diarylnitroxides: Photochemical tests

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ARTICLE INFO

Article history:
Received 31 May 2018
Revised 26 June 2018
Accepted 2 July 2018
Available online 3 July 2018

Keywords:
Diarylnitroxides
Photodegradation
Photochemical stability
Quantum yield

ABSTRACT

Photochemical stability and possible routes for photodegradation of twisted diarylnitroxides were determined. It was shown that quantum yields for twisted diarylnitroxides fall in the range typical for the best representatives of alkylnitroxides providing an additional support that twisting of the phenyl ring from the N-O conjugation plane constitutes an efficient route for increasing thermo and photo stability of the nitroxides.

Introduction

Stable nitroxide radicals are widely used in various areas: as redox mediators, radical traps, spin labels and probes, antioxidants, redox active electrode materials, etc. [1,2]. Wide spectrum of practical applications of nitroxides listed above requires new compounds with precisely adjusted properties, e.g., stability, redox-potential values, solubility, etc. Consequently, targeted structural design of molecules for certain application is of primary importance. Commonly used stable alkylnitroxides (the most popular is TEMPO – 2,2,6,6-tetramethylpiperidine-1-oxyl – and its derivatives) are not too sensitive to structural modification since electron transfer via σ – bonds is less efficient than via π-conjugation. From this point of view, diarylnitroxides are more preferable. However, arylnitroxides are commonly insufficiently stable. Contrary to the aliphatic compounds in which the spin density is located at the nitroxyl group, the spin density in arylnitroxides is delocalized over the *ortho*/*para* positions of aromatic rings [3,4]. Such delocalization provides additional reaction centers and initiates unwanted reaction channels thus decreasing stability.

Recently, new strategy for molecular design of stable diaryl nitroxides was suggested [5,6] and a broad series of new twisted diarylnitroxides containing a bulky substituent in the *ortho*-position in the phenyl ring was obtained. Principal idea of structural design was in removing one aryl moiety from the conjugation with the nitroxyl radical center (thus preventing spin density delocalization over the phenyl ring) whereas the other aryl ring should stay conjugated. This allows obtaining a smart tunable system with the increased stability (both thermodynamic and kinetic) not only of the radical species but of their oxidized and reduced forms as well [4]. New approach broadens the scope of available stable diarylnitroxyl radicals which are practically important.

The present paper is further development of this research. It is aimed at quantitative estimation of the photochemical stability of twisted arylnitroxides and their comparison with previously known relatively stable nitroxide radicals of diaryl and dialkyl type. Since some of twisted diarylnitroxides can stay for weeks in benzene solution in an open air without light protection at room temperature without any noticeable destruction, more harsh conditions were applied (laser light, wavelength 405 nm, intensity $5 \cdot 10^{-9}$ Einstein/s per sample) to get reliable quantitative data. The structure/stability relationship will be established for the radicals to demonstrate the role of twisting in their stabilization. Possible routes for photochemical degradation of diaryl nitroxides will be also discussed. It should be mentioned that photochemical degradation of dialkylnitroxides has been previously reported in a number of publications [7–11] whereas photochemical stability of diaryl derivatives has drawn little attention [12].

Results and discussion

For the investigation, a number of diarylnitroxides with bulky *tert*-butyl and trifluoromethyl substituents in the phenyl rings were chosen (Scheme 1) and synthesized. Radicals **1**–**5** were chosen to reveal an influence of the electronic nature of the substituents as well as their location on the stability and photoinduced degradation routes. Twisted nitroxides **1**–**3** will be compared with their planar counterparts **4** and **5**.

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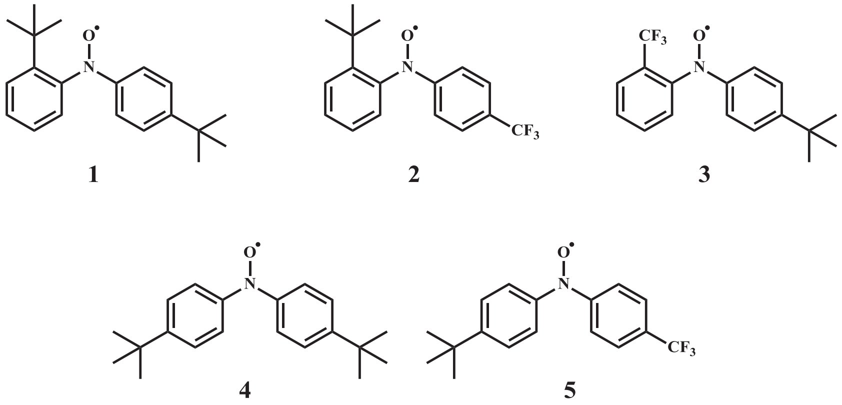
https://doi.org/10.1016/j.tetlet.2018.07.007
0040-4039/



Scheme 1. The diarylnitroxides under investigation.

Radicals **1**–**5** are stable in crystal form; they stay for months in an open air without any noticeable destruction. As concerns the radicals' life time in solution, preliminary estimation using spin counting method showed that the sample of 2-^{t}Bu,4′-CF_3-diphenyl nitroxide stayed for more than two weeks in benzene solution in an open air at room temperature without protection of the light and exhibited the amount of radical species which was almost 100% of the starting value. Encouraged with this result, we performed more detailed quantitative research on photochemical stability of radicals **1**–**5** in toluene solution. Toluene seems to be an optimal solvent for estimating the inherent stability of the radicals toward decomposition since it is not prone to initiate secondary radical transformations.

To determine the quantum yields of photochemical decomposition of radicals **1**–**5**, the irradiation with near-UV laser light (wavelength 405 nm, intensity $5{\cdot}10^{-9}$ Einstein/s per sample) was carried out. The following kinetic model of photochemical radical decomposition was used:

$$\frac{dN}{dt} = I_0(1 - 10^{-A(t)})\varphi$$

where N is the number of radical molecules, I_0 is light intensity, φ is the quantum yield of the reaction, $A(t)$ is absorbance of the solution at the irradiation wavelength, which was calculated by Bouguer–Lambert–Beer's law$A(t) = \frac{\varepsilon_{405} l}{V} \cdot N(t)$,where ε_{405} is extinction coefficient on the irradiation wavelength, l is the optical path length of irradiating light, and V is the sample volume.

In equation given above the value $I_0(1 - 10^{-A(t)})$ is the number of photons absorbed by radical molecules per unit time, and the expression $\Delta(t) = \int_0^t I_0(1 - 10^{-A(\tau)})d\tau$ represents the absorbed irradiation dose. According to equation, the slope of the curves of $N(t)$ against $\Delta(t)$ gives the quantum yield of photochemical decomposition of the radicals [13].

The quantum yields of photochemical decomposition of radicals **1**–**5** measured as described above are given in Table 1. This table also lists extinction coefficients ε of the radicals at the irradiation wavelength, and the product $\varepsilon \cdot \varphi$, which is proportional to the apparent rate constant of photochemical reaction in the limit of low absorbance. Some literature data obtained for other types of nitroxides are also given in Table 1 for comparison. If the data in toluene were not available in literature, the results measured in other hydrocarbons (benzene or pentane) were taken. These solvents are close in polarity and do not provoke radical transformations, similar to toluene. Thus, one can expect that such comparison will not lead to any uncertainty in the conclusions.

As follows from the data presented in Table 1, twisted diarylnitroxides **1** and **2** are significantly more stable under laser irradiation than planar di-*para*-substituted analogues, in spite of a vacant *para*-position in one ring. Interestingly, electronic nature of substituents does not affect photodegradation efficiency (entries 1, 2 in Table 1) whereas the dihedral angle turned out to be a crucial point. One can see that nitroxide **3** is destabilized as compared to 4,4′-disubstituted compounds, contrary to twisted nitroxides **1** and **2**. The reason is much smaller dihedral angle which does not block the conjugation with NO moiety completely (52.2° in case of **3** vs. 69.8° and 67.4° for **2** and **1**) due to less bulky trifluoromethyl group in the *ortho* position. This provides a certain spin

Table 1

Quantum yields of decay of radicals 1–5 (toluene, 298 K, 405 nm, intensity $5{\cdot}10^{-9}$ Einstein/s per sample) and some literature data for comparison.

	Substituents in the phenyl rings	Solvent	Irradiation wavelength λ, nm	Quantum yield, φ	Extinction coefficient, ε, $M^{-1}{\cdot}cm^{-1}$	$\varepsilon \cdot \varphi$, $M^{-1}{\cdot}cm^{-1}$	Reference
1	2,4′-di ^{t}Bu	toluene	405	$4{\cdot}10^{-3}$	650	2.6	present work
2	2-^{t}Bu,4′-CF_3	toluene	405	$5.5{\cdot}10^{-3}$	400	2.2	present work
3	2-CF_3,4′-^{t}Bu	toluene	405	$1.3{\cdot}10^{-2}$	1350	17.55	present work
4	4,4′-di-^{t}Bu	toluene	405	$8{\cdot}10^{-3}$	1200	9.6	present work
5	4-^{t}Bu,4′-CF_3	toluene	405	$8{\cdot}10^{-3}$	1350	10.8	present work
6	4,4′- OCH_3	benzene	436	$8{\cdot}10^{-3}$	~1000	8	[12]
7	TEMPO	heptane	436	$<6{\cdot}10^{-4}$	~10	$<6{\cdot}10^{-3}$	[8]
		CCl_4	365	$4.8{\cdot}10^{-1}$	–*	–	
8	di-*tert*-butyl-nitroxide	pentane	254	$2.1{\cdot}10^{-1}$	~2500	525	[7]
9	nitronyl nitroxide	benzene	578	$9.8{\cdot}10^{-3}$	–*	–	[14]
			313	$1.3{\cdot}10^{-2}$	–*	–	
10	2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-1-oxyl**	toluene	365	$1.6{\cdot}10^{-1}$	55	8.8	[9]

[*] Data on extinction coefficient were not provided in the corresponding reference.