

## Short Communication

## Hydrogen abstraction in the photolysis of aromatic nitroso spin traps

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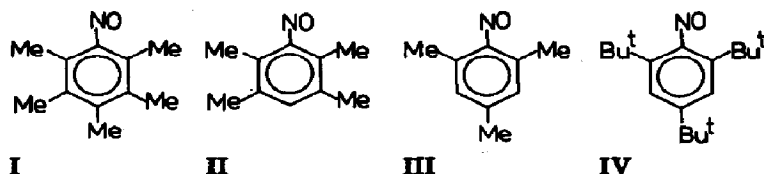
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Unlike nitrosoalkanes, which readily undergo C—NO bond homolysis [1], sterically hindered aromatic nitroso compounds such as pentamethylnitrosobenzene I [2], 2,3,5,6-tetramethylnitrosobenzene (nitrosodurene) II [3], 2,4,6-trimethylnitrosobenzene (nitrosomesitylene) III [4] and 2,4,6-tri-*tert*-butylnitrosobenzene IV [5] are considered to be photochemically stable and, therefore, are recommended as spin traps for the study of photo-reactions.



However, it has been reported [6] that upon photolysis with UV light IV undergoes a series of chemical reactions caused by C—NO bond cleavage. Inadvertent photolysis rather than molecule-assisted homolysis has been shown [7] to be the origin of numerous examples of "spontaneous" nitroxide formation reported in the literature.

Despite the claimed photostability of II [3], similar reactions are also believed to occur for this compound [7]. However, no experimental evidence supporting this suggestion has been provided so far.

We have performed electron spin resonance (ESR) studies on the photochemical behaviour of the sterically hindered aromatic nitroso spin traps I - III in various solvents (see Table 1). Fairly intense ESR signals of nitroxides have been detected upon photolysis ( $330 \text{ nm} < \lambda < 500 \text{ nm}$ ). These signals may be unambiguously assigned to nitroxides formed by hydrogen abstraction from the solvent and subsequent spin trapping of these radicals. No radicals were detected upon excitation of the  $n\pi^*$  transition (at about 800 nm) of the monomeric nitroso compound. Molecular oxygen

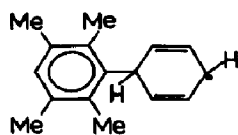
TABLE 1

Nitroxides formed during photolysis of aromatic nitroso spin traps<sup>a</sup>

Spin trap	Solvent	Radical added	$a_N$ (mT)	$a_H$ (mT)
I	Toluene	$\cdot\text{CH}_2\text{C}_6\text{H}_5$	1.346	0.805 (2H)
II	Toluene	$\cdot\text{CH}_2\text{C}_6\text{H}_5$	1.357	0.785 (2H)
II	<i>n</i> -Heptane	$\cdot\text{CH}(\text{CH}_3)\text{C}_5\text{H}_{11}$ <sup>b</sup>	1.330	0.658 (1H)
II	Cyclohexane	Cyclohexyl	1.360	0.690 (1H)
II	<i>p</i> -Xylene	$\cdot\text{CH}_2(4\text{-CH}_3\text{C}_6\text{H}_4)$	1.327	0.766 (2H)
II	( $\text{C}_2\text{H}_5$ ) <sub>2</sub> O	$\cdot\text{CH}(\text{CH}_3)\text{OC}_2\text{H}_5$	1.294	0.640 (1H)
III	Toluene	$\cdot\text{CH}_2\text{C}_6\text{H}_5$ <sup>c</sup>	1.335	0.777 (2H)

<sup>a</sup>0.01 M spin trap, deoxygenated solutions; all coupling constants  $\pm 0.005$  mT.<sup>b</sup>Tentatively assigned.<sup>c</sup>Spin adduct of the mesityl radical has been detected also ( $a_N = 1.014$  mT;  $a_H^1 = 0.124$  mT (3H);  $a_H^2 = 0.082$  mT (6H);  $a_H^3 = 0.074$  mT (2H)).

was found to act as an efficient quencher for the formation of the nitroxides. In accordance with previous reports [2 - 4] only extremely weak ESR signals were recorded in benzene solution. However, it should be noted that samples prepared according to the procedures described in ref. 8 may contain traces of acetoxymercuri aromatics, which give rise to ESR signals upon photolysis. Thus, the photolysis of acetoxymercuridurene in benzene leads to diduryl nitroxide in the presence of II ( $a_N = 1.025$  mT;  $a_H^1 = 0.108$  mT (2H);  $a_H^2 = 0.072$  mT (6H);  $a_H^3 = 0.036$  mT (6H) [9]) together with a nitroxide ( $a_N = 1.33$  mT;  $a_H = 0.86$  mT) which has been tentatively assigned to the spin adduct of the durylcyclohexadienyl radical V formed by addition of duryl radicals to benzene [10].



V

Using the photolysis of acetoxymercuridurene as a convenient source for duryl radicals we were able to demonstrate that duryl radicals may act as hydrogen abstractors. Therefore, rather than photoexcited nitroso aromatics, duryl radicals formed by photoinduced C—NO bond cleavage are responsible for the hydrogen abstraction from the solvent molecules. Moreover, no aryl hydronitroxides ( $\text{ArN}(\text{O}^\cdot)\text{H}$ ) or nitroso anion radicals were detected during the photolysis of aromatic nitroso spin traps which, however, should be formed if the photoexcited nitroso compound undergoes hydrogen abstraction or electron transfer with the solvent.

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