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PENTAMETHOXYNITROSOBENZENE : $(MeO)_5PhNO$. A USEFUL NEW SPIN-TRAPPING AGENT

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Summary : *Pentamethoxynitrosobenzene (PMeONB) has been prepared and its use as a spin-trapping (ST) agent has been investigated. Its solubility is adequate for ST in most organic solvents ; compared with the routinely used aryl nitroso compounds, PMeONB is more dissociated into the active monomeric form in solution ; the potential windows are of the same order of magnitude. Its spin adduct ESR spectra give more information on the trapped radical than those of any other ST agent.*

Aliphatic and aromatic nitroso compounds have been widely used as spin-trapping (ST) agents for the spin-trapping technique[1], whereby short-lived free radicals in a reaction system attach themselves the trapping agents to form persistent nitroxide (or anilino-type) radicals, which are indirectly identified by means of conventional electron spin resonance (ESR) measurements.

$$R\bullet \; + \; R'NO \longrightarrow RN(\dot{O})R'$$

The success and the value of a ST experiment depend on a certain number of features[1] including a good resolution (high signal to noise ratio and small linewidth) of the spin adduct ESR spectrum for clearly identifying the trapped radical R• .
Arylnitroso compounds are the most commonly used ST agents. Nitrosobenzene is fairly reactive toward free radicals, however a drawback of this ST agent is that its spin adduct ESR spectra, because of the ring protons, show complex hyperfine structures that make the identification of the trapped radicals questionable.
Substitution of the ring protons with alkyl groups (mainly methyl) has been used to simplify the hyperfine structure of the spin adduct ESR spectra[2]. However, owing to unresolved splittings, the presence of alkyl groups on the ring dramatically increases the apparent linewidth, thus reducing the amount of information that can be obtained on the trapped radical. We have found that this significant disadvantage in the use of alkyl-substitued aryl nitroso ST agents can be avoided by using PMeONB. The present report describes several aspects of PMeONB as a ST agent.

Results and Discussion : According to the general method for the synthesis of aromatic nitroso compounds[3], pentamethoxybenzene[4] is converted into $C_6(OMe)_5HgOAc$, in ca 60% yield. It is then converted into PMeONB upon treatment with nBuONO in acidic medium. The yield of the nitrosation step is ca 80%. The PMeONB is purified by recrystallization from 50:50 chloroform-methanol (mp : 128 °C). An X-ray diffraction study[5] of a crystal of this product has shown it to be the dimeric form of PMeONB with measured bond lengths and angles very close to those reported for other dimeric arylnitroso compounds[6].
PMeONB is partially dissociated into the monomeric form in solution and sufficient concentrations (0.02 M - 0.05 M) for spin-trapping were readily obtained in most solvents at room temperature.

We and others[7] have pointed out the possibility for arylnitroso compounds to be involved in electron-transfer processes during the course of a ST experiment. Accordingly, the redox behavior of the ST agent is a very important aspect to be taken into account when a ST experiment is considered.
We have found that the monomeric form of PMeONB is reduced at -1.40 V and oxidized at 0.90 V (CH_3CN, Stationary Pt disk. Reference $Ag/AgNO_3$, 0.01 M). The reduction step is reversible and the radical anion PMeONB is easily detected by ESR (A_N = 7.93 G, g = 2.0068). The oxidation step is partially reversible (potential sweep rate 50 mV s^{-1}) and the radical cation $PMeONB^+$ can be detected in very thoroughly dried acetonitrile (A_N = 34.1 G, $A_H(3H)$ = 0.7 G, g = 2.0034). Pulsed valtametry was used[8] to obtain the dissociation constants KD for the dimer-monomer equilibrium for a series of arylnitroso compounds. KD was found to be 1.12×10^{-3} for PMeONB and the active monomeric form is approximately two times greater with PMeONB than with nitrosodurene or pentamethylnitrosobenzene[9].

Table 1 summarizes the observed ESR parameters at room temperature for a number of adduct radicals generated from short-lived free radicals and PMeONB in benzene.
The nitroxides formed by trapping alkyl radicals exhibit the same overall pattern as those obtained using nitrosodurene as a ST agent. However, the PMeONB spin adducts give ESR spectra that are much better resolved than those of the nitrosodurene or 1,2,4,5-tetrakis (trideuteriomethyl)nitrosobenzene (DND)[2] spin adducts. This very important advantage of PMeONB over nitrosodurene or even DND is clearly illustrated by comparing the ESR spectrum obtained by trapping the allyl radical with PMeONB (Fig. 1B) with that obtained through trapping with DND (Fig. 1A).
Kinetic studies of ST with PMeONB and the synthesis of water soluble polyalkoxynitrosobenzene ST agents are in progress in our laboratory.

Table 1 : ESR parameters (Gauss, room temperature, benzene) for several spin adducts formed from pentamethoxynitrosobenzene.

Trapped radical	Radical source	PMeONB present results		Nitrosodurene by Terabe et al[2]	
		A_N	A_H and others	A_N	A_H
$\bullet CH_3{}^{a}$	A	13.1	11.8(3H)	13.7	12.17(3H)
$\bullet CH_2CH_3$	A	12.9	9.7(2H),0.35(3H)	13.68	10.97(2H)
$\bullet CH_2(CH_2)_2CH_3$	A	12.9	9.5(2H),0.35(2H)		
$\bullet CH_2Ph$	A	12.8	8.7(2H)	13.61	7.93(2H)
$\bullet CH_2CH = CH_2$	A	12.8	9.2(2H),0.47(1H)^{c} 0.19(2H)^{c}	13.57	10.20(2H)
$\bullet CHMe_2$	A	13.3	4.5(1H),0.28(6H)	13.72	6.92(1H)
•Cyclohexyl	A	13.1	4.7(1H),0.7(6H)^{c}	13.57	6.93(1H)0.14(?)
$\bullet C(CH_3)_3$	A	13.5	0.27(9H),7.7(1 ^{13}C) 4.1(3 ^{13}C)	13.60	0.17(?)
•Adamantyl	A	13.4	0.5(9H)		
$\bullet C(CN)Me_2$	AIBN(50°C)	13.1	0.3(6H)	13.14	0.18(?)
$\bullet Ph^{b}$	$(PhCO)_2O$(50°C)	10.0	2.7(H_o,H_p),0.94(Hm)	10.11	0.95(Hm)
•CH(OH)Me	EtOH+DBPO	13.0	5.0(1H),0.3(1H,OH)	13.86	6.88(1H)
•SEt	EtSH+DBPO	14.4	(g value 2.0067)		
$\bullet SCh_2Ph$	$PhCH_2SH$+DBPO	14.3	(g value 2.0067)		
•C(O)iPr	iPrC(O)H+DBPO	7.3	(g value 2.0069)		
•C(O)Et	EtC(O)H+DBPO	7.3	(g value 2.0069)		
$\overset{-}{\bullet}BH_3{}^{d}$	$NaBH_4$	12.6	12.1(3H) 5.7(^{11}B)		

A : RBr + BU_3SnH + DBPO, DBPO : di t-Butylperoxalate, a : all the nitroxides corresponding to the trapping of alkyl radicals have g value 2.00060±0.0002, b : g = 2.0058, c : spectrum simulation. d : M.P. Crozet and P. Tordo, J. Am. Chem. Soc. ; 102, 5696, 1980.

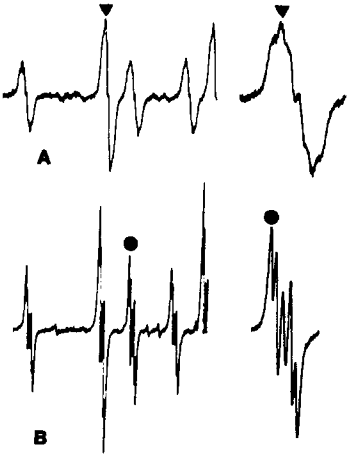

Fig. 1 : Half spectra of the nitroxydes obtained by trapping the allyl radical (A) with DND (B) with PMeONb.

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