CHEMISTRY LETTERS, pp. 115-118, 1972. Published by the Chemical Society of Japan

SPIN TRAPPING BY USE OF NITROSO COMPOUNDS. III.[1] PHENOXAZINE-N-OXYL PRODUCED FROM THE PHENOXY RADICAL BY SPIN TRAPPING

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Phenoxazine-N-oxyl was produced from the phenoxy radical in the ESR spin trapping technique using nitrosobenzene, and the mechanism of formation was deduced from the results of trapping using deuterated compounds and by product analysis.

The unique diagnosis of short-lived free radical intermediates by electron spin resonance trapping techniques ("spin trapping") has recently received wide attention.[2] Both nitroso compounds[3] and nitrones[4] react readily with organic radicals to form relatively stable nitroxide radicals. We recently applied this technique using nitroso compounds to detect and identify free radicals in oxidation reactions of active hydrocarbons and amines with nickel peroxide (Ni-PO).[5] Leaver, Ramsay, and Suzuki reported that the phenoxy radical generated in the photolysis of phenol was trapped by 2-methyl-2-nitrosopropane to produce phenoxy t-butyl nitroxide.[6] In this paper, we report the identification of an unusual nitroxide encountered in an investigation of the oxidation of phenol with Ni-PO by the spin trapping method using nitrosobenzene, and the mechanism of formation of this nitroxide is discussed. It is known that the reactions of phenols with Ni-PO afford the one electron oxidation products.[7]

Phenol (0.05 M) was oxidized with Ni-PO (2 equiv. amounts of the substrate) in the presence of nitrosobenzene (0.1 M) in deoxygenated benzene at room temperature, and the ESR spectrum was immediately measured by a Varian V4502-15 EPR spectrometer to obtain the spectrum shown in Figure 1. In the absence of Ni-PO, only the weak signal of phenyl nitroxide was observed. Analysis of this spectrum (Table 1) suggests that this radical is not phenyl phenoxy nitroxide formed by attacking of the oxy radical to the nitrogen atom, but phenoxazine-N-oxyl, as obtained by Scheffler and Stezmann[8] in the oxidation of phenoxazine with t-butyl hydroperoxide.

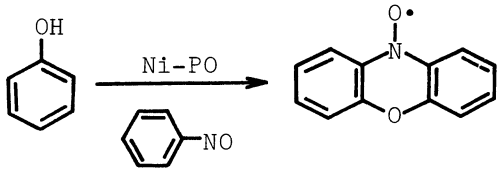
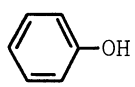
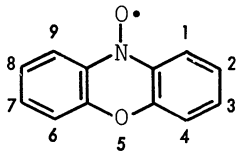
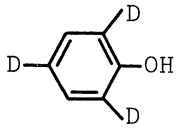
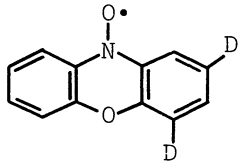
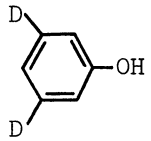
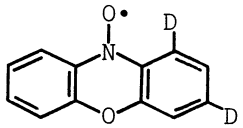
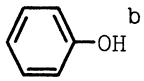
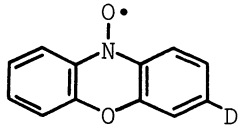
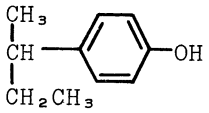
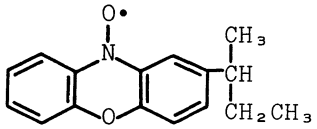


Table 1. Spin Adducts by Nitrosobenzene in the Oxidation of Phenols with Nickel Peroxide[a] (Gauss)

Phenols	Nitroxides	a_N	a_{H_1}	$a_{H_{2,4}}$	a_{H_3}	$a_{H_{6,8}}$	a_{H_7}	a_{H_9}
		9.20	2.36	0.46	2.48	0.46	2.48	2.36
		9.20	2.37	0.07(D)	2.47	0.46	2.47	2.37
		9.20	0.37(D)	0.46	0.37(D)	0.46	2.49	2.39
 b)		9.20	2.36	0.46	0.38(D)	0.46	2.46	2.36
		9.30	2.30[c]	0.45[d]	2.56	0.45	2.56	2.40[c]

a) In benzene at room temp. b) p-Deuterionitrosobenzene was used. c) Assignment is uncertain.
d) $a^H_{2\text{-}CH} = 0.15$.

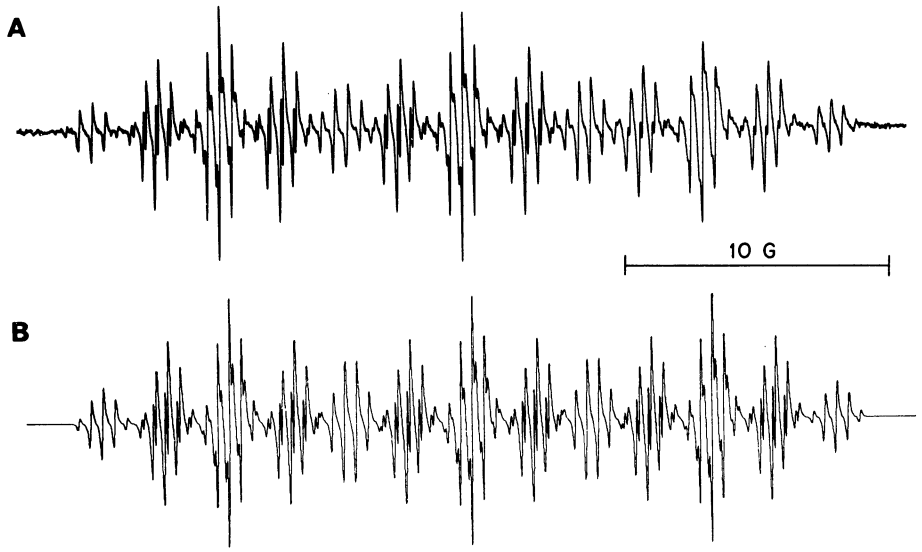
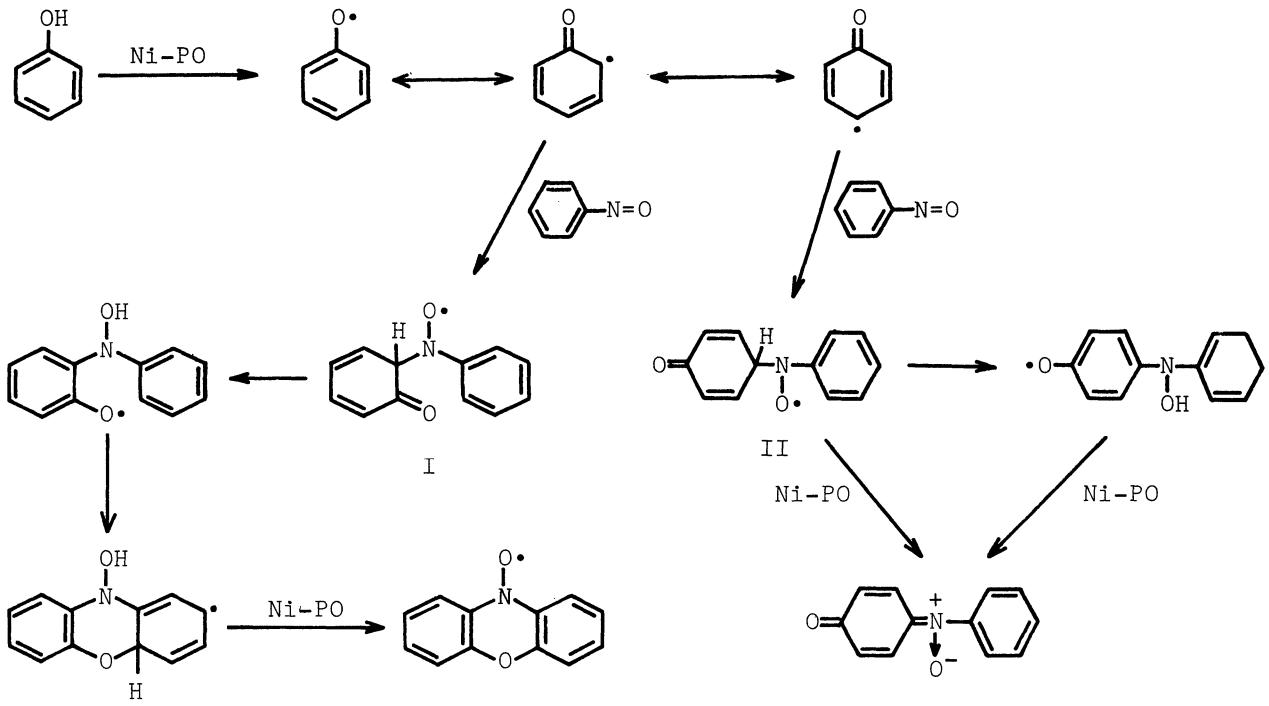


Figure 1. A: ESR spectrum of phenoxazine-N-oxyl in benzene at room temperature.
B: A simulated spectrum.

In order to identify this radical and to elucidate the reaction mechanism, deuterated phenols and an alkyl substituted phenol were used instead of phenol itself. From the results shown in Table 1, we conclude that the nitroxide radical obtained by spin trapping of the phenoxy radical with nitrosobenzene is phenoxazine-N-oxyl. Furthermore, by preparing 3-deuteriophenoxazine-N-oxyl using p-deuterionitrosobenzene as a spin trap, it was clarified that the hyperfine coupling constants of 1-H and 9-H are smaller than those of 3-H and 7-H, although the values in these positions are ambiguous in the literature.[8] No benzyl nitroxide derivative was observed on oxidation of p-(α-methylpropyl)phenol, despite the report by Leaver and Ramsay that 3,5-di-t-butyl-4-hydroxybenzyl t-butyl nitroxide was obtained during photolysis of benzophenone in the presence of 2,6-di-t-butyl-4-methylphenol and 2-methyl-2-nitrosopropane.[9]

On the other hand, in the reaction of phenol and nitrosobenzene in the presence of Ni-PO, a red crystalline product was isolated (recrystallization from water after separation by PLC: mp 143°C). This was identified as N-phenyl p-quinoneimine N-oxide, based on the physical data for an authentic sample prepared by the oxidation of p-anilinophenol with mercuric oxide followed by oxidation with m-chloroperbenzoic acid.

Consequently, it is presumed that the reaction path of this trapping is explained by the following scheme.



The primary spin adducts, hexadienyl nitroxides (I, II), were not observed probably because of unstability of these nitroxides.

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(Received November 24, 1971)