

ARYL-NITROSO-AMINYLOXIDE, ARYL-TOSYL-AMINYLOXIDE, AND DIARYL-AMINYLOXIDE,
WHERE THE ARYL IS 3,5-DI-t-BUTYLPHENYL

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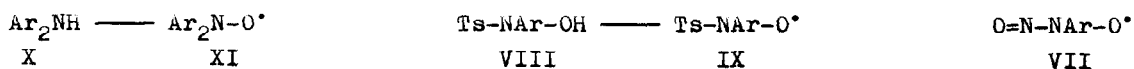
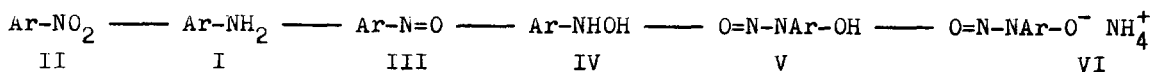
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The ESR spectra of phenyl-substituted free radicals are considerably simplified if the meta-protons (affording the smallest coupling constants) are replaced by t-butyl groups.¹⁻³ Additionally, these groups prevent reactions at the adjacent aromatic positions involved in the decomposition of these free radicals, increasing thereby their persistence.

It was shown earlier⁴ that N-tosyl-N-phenylhydroxylamine (VIII, Ar = Ph) was oxidized to radical IX, Ar = Ph, which afforded slowly radical VII, Ar = Ph, which decomposed in turn yielding diphenyl-aminyloxide (diphenyl-nitroxide⁵), XI, Ar = Ph. Radical VII, Ar = Ph could be also obtained by two other pathways: spin trapping of NO by nitrosobenzene, and oxidation of cupferron (VI, Ar = Ph) with lead tetraacetate.^{4,6} The ESR spectra of this radical VII, Ar = Ph^{4,6} or of related p-substituted derivatives⁷ could be analyzed, but are rather complex.⁸

3,5-Di-t-butylaniline^{1,3,9} (I, henceforth Ar will be 3,5-di-t-butylphenyl unless otherwise specified) was oxidized by hydrogen peroxide in acetic acid to 3,5-di-t-butylnitrobenzene II, but attempts to convert this into VI failed. Therefore I was converted into 3,5-di-t-butylnitrosobenzene III,³ and this was reduced to 3,5-di-t-butyl-phenylhydroxylamine IV.³ Nitrosation of IV with sodium nitrite in aqueous-ethanolic hydrochloric acid afforded 3,5-di-t-butyl-N-nitroso-phenylhydroxylamine V, which on treatment with gaseous ammonia in ether yielded 3,5-di-t-butyl-cupferron VI.



Oxidation with lead tetraacetate in dioxane converted VI into 3,5-di-t-butyl-N-nitroso-phenyl-aminyloxide VII, which was stable in deaerated solution at

room temperature for several days. The ESR spectrum of VII can be described as consisting of 29 equally spaced lines with intensities 1:0:3:1:3:3:2:3:4:1:6:1:4:3:2(centre line):... If the interval between two successive lines is denoted by d , this ESR spectrum can be decomposed into three equally intense multiplets centered at the lines with intensities 2, yielding $a_{N-O} = 8d$. Each multiplet has 13 equally spaced lines with intensities 1:0:3:1:3:3:2:3:3:1:3:0:1. On looking into the table of all theoretically possible ESR spectra with equidistant lines,¹⁰ the above multiplet is unambiguously found to arise from the interaction of the odd electron with one ^{14}N and three ^1H nuclei, provided that $a_{\text{H}} = 2d$ and $a_{\text{N}} = 3d$. The ESR spectrum can thus be simulated with three hyperfine coupling constants : $a_{N-O} = 10.2$ G, $a_{N=O} = 3.75$ G, and $a_{\text{H}} = 2.53$ G for the ortho and para protons, yielding intensities very close to the experimental ones. The g -value is 2.0055.

Treatment of IV with *p*-toluenesulphonyl chloride in benzene yielded the crystalline tosylate VIII which on oxidation with lead tetraacetate in benzene afforded 3,5-di-*t*-butyl-*N*-tosyl-phenyl-aminyl-oxide IX with an ESR spectrum consisting of a 1:1:1 triplet of 1:3:3:1 quadruplets due to $a_{\text{N}} = 11.7$ G and $a_{\text{H}} = 1.71$ G for the o- and p-protons. The g -value is 2.0051 ± 0.0001 .

The bis(3,5-di-*t*-butylphenyl)aminyl-oxide XI was not formed at room temperature from VII (as it happened with Ar = Ph), but could be prepared by heating $\text{Ar}_2\text{NH} (X)^1$ with 30% hydrogen peroxide in acetic acid ; precipitation with water gave XI, whose ESR spectrum in benzene consisted of a 1:1:1 triplet of partly overlapping 1:6:15:20:15:6:1 septets, due to $a_{\text{N}} = 9.74$ G and $a_{\text{H}} = 1.83$ G (for the six o- and p-protons). This radical is stable both as a solid, and in deaerated benzenic solution at room temperature. Its g -value is 2.0051 ± 0.0001 .

The coupling constants obtained from the simple ESR spectra of the persistent free radicals VII, IX, and XI, agree with those of the analogous radicals with Ar = Ph, confirming thus the earlier assignments.^{4,6-8} The enhanced stability of the new free radicals is due to the steric effects of the *t*-butyl groups.

FOOTNOTES AND REFERENCES

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5. The traditional name "nitroxide" should be replaced by "aminyl-oxide" or "aminoxyl".
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