# Stable Free Radicals Derived from 4-Arylazo-2,6-di-*t*-butylphenols

Eiichiro MANDA

*Government Chemical Industrial Research Institute, Tokyo, Honmachi, Shibuya-ku, Tokyo*

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It is well known that 2,6-di-*t*-butylphenol derivatives give stable phenoxy radicals (I) by oxidation.[1]

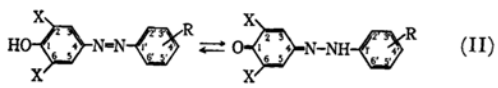
(I) X: *t*-butyl

In this study, 4-arylazo-2,6-di-*t*-butylphenols (II) were synthesized, and stable radicals were derived from them by KOH-$K_3Fe(CN)_6$ oxidation.

Seven derivatives of II were prepared from 2,6-di-*t*-butyl-*p*-benzoquinone and the corresponding arylhydrazine hydrochlorides by letting the aqueous-alcoholic reaction mixtures stand for five days at room temperature. The seven derivatives were as follows: R=4′-methoxy (II-A); R=4′-methyl (II-B); unsubstituted (II-C); R=4′-chloro (II-D); R=4′-nitro (II-E); R=2′,4′-dinitro (II-F); R=2′,4′,6′-trinitro (II-G).

II-A, II-B, II-C, II-D, and II-E give a sharp OH absorption at 3670 $cm^{-1}$, but no NH absorption at 3300 $cm^{-1}$ in benzene, and *vice versa* with II-F and II-G. Almost all the derivatives show two absorption maxima, near 360 m$\mu$, and 450 m$\mu$, in benzene (II-G shows only one peak, at 425 m$\mu$), but their molecular coefficients vary with the substituents.

From the above data, it can be concluded that II-G exists exclusively in the hydrazone form, but the other six compounds show azo-hydrazone tautomerism in benzene.[2]



(II)

azo-form hydrazone-form

When the benzene solutions of II were treated with a large excess of an aqueous KOH-$K_3Fe(CN)_6$ solution, the benzene layers turned red immediately. After having been shaken for three minutes, the benzene layers were washed and degassed with cooling by dry ice and methanol, and then the ESR spectra were measured as soon as possible.

All the samples gave ESR signals, and the signals remained for a few days at room temperature in a sealed tube. The lifetimes of the radicals were three days (II-A, II-B, II-D, II-E), one day (II-C), and more than ten days (II-F, II-G).

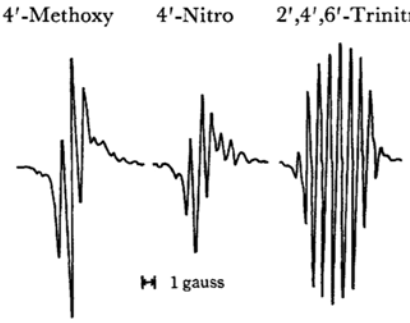



Fig. 1. Some ESR spectra of free radicals derived from II.

With the exception of II-G, the shapes of the ESR spectra suggest that two radical species exist in the sample solution. It is considered that the one species, which gives three lines, is derived from azo-tautomer, and the other, which gives nine lines, is derived from hydrazone-tautomer.

The details will be reported in the future.

1) E. A. Altwicker, *Chem. Revs.*, **67**, 475 (1967).

2) K. J. Morgan, *J. Chem. Soc.*, **1961**, 2151.