

SPIN TRAPPING IN PHOTOLYSIS OF  
DI-PHENYLACETATO(2,9-DIMETHYL-1,10-PHENANTHROLINE)COPPER(II)<sup>1</sup>

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Copper(II) complexes with sterically hindered aromatic 1,2-diimines are known to be unstable toward irradiation with UV light.

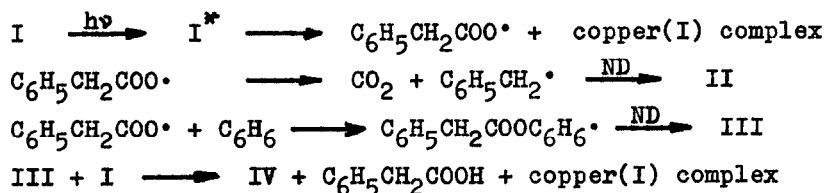
Although a mechanism via free radicals seems to be probable<sup>2</sup>, there is no direct evidence for intermediate free radicals.

Using spin trapping technique (with nitrosodurene, ND, as a spin trap<sup>3</sup>) we were able to detect the intermediate radicals in photo-reduction of di-phenylacetato(2,9-dimethyl-1,10-phenanthroline) - copper(II), I, by esr.

In situ UV irradiation of 0.01 M benzene solution of I in the presence of ND (0.005 M) produced a nitroxide radical whose esr parameters ( $a_N=1.36\pm 0.015$  mT,  $a_H=0.825\pm 0.015$  mT (2H)) are very close to those reported<sup>3</sup> for the benzyl duryl nitroxide, II. At higher (0.02 M) concentrations of the spin trap some additional lines of rather low intensity ( $a_N=1.36\pm 0.03$  mT,  $a_H=0.73\pm 0.03$  mT (1H)) could be observed. Probably these lines are arising from a radical III which is formed by addition of the benzyl carboxyl radical to benzene followed by the trapping of the resulting cyclohexadienyl radical by ND<sup>4</sup>. The amount of III observed in the esr spectrum was

about 5% of II only. The trapping of benzyl radicals by benzene can be rejected since under the same conditions the photolysis of benzyl iodide gave no cyclohexadienyl radicals.

When irradiation was stopped the signal of II decayed with a half-life time of 45 s. The signal of III completely disappeared within 10 s and was replaced by another spectrum ( $a_N=1.02\pm 0.02$  mT,  $a_H=0.28\pm 0.02$  mT (2H), and additional poorly resolved splitting of about 0.09 mT by two protons). We attribute this spectrum to the p-substituted phenyl duryl nitroxide IV which is formed by oxidation of III by I. In chloroform solution the only radical observed was the benzyl duryl nitroxide II ( $a_N=1.395\pm 0.015$  mT,  $a_H=0.87\pm 0.015$  mT (2H) ). On the basis of these results the following mechanism for the photoreduction of the complex I may be derived.



### Experimental

All experiments have been made in deaerated solutions. The irradiation was performed within the esr cavity of a JES-3BQ (Jeol) spectrometer at room temperature. The copper complex I was prepared by a method described in ref.<sup>5</sup>.

### References and Note

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