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C-NITROSO COMPOUNDS. PART XXII

THE MECHANISM OF PHOTOCHEMICAL NITROXIDE FORMATION FROM NITROSO-MONOMERS

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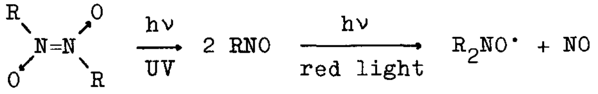
In earlier work from our laboratory it was shown that dimeric nitroso compounds must first be dissociated either thermally or photochemically (UV) into monomer before they can be transformed to nitroxides by red light (1,2,3).



So far the details of the second step have not been elucidated.

A priori there are two possibilities:

a) A collision between a long lived excited nitroso monomer and a second (monomeric) molecule with concomitant formation of the nitroxide.

$$RNO \xrightarrow{h\nu} RNO^{*}$$

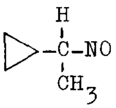
$$RNO^{*} + RNO \longrightarrow R_2NO^{\cdot} + NO$$

b) Photodissociation of the C-NO bond, followed by scavenging of the alkyl radical by a second (non-excited) nitroso alkane.

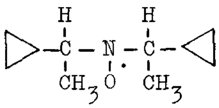
$$RNO \xrightarrow{h\nu} RNO^{*} \longrightarrow R^{\cdot} + NO$$

$$R^{\cdot} + RNO \longrightarrow R_2NO^{\cdot}$$

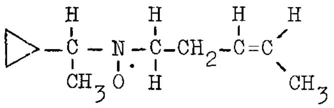
In order to make a decision between these alternatives we have now studied the photolysis of 1-cyclopropyl-1-nitrosoethane (I) (4) in toluene. If the nitroxide formation takes place via mechanism a) this compound should give a nitroxide II with two equivalent β-hydrogens. In fact we find an ESR signal with hfs from three hydrogens i.e. a_H = 4.8 gauss (1H) and 9.5 gauss (2H).



I



II (not observed)

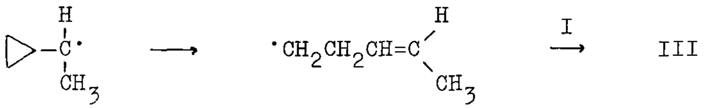


III (observed)

The a_N value of 14.1 gauss is characteristic for a dialkylnitroxide.

These observations lend strong support to mechanism b) for the following reasons. From the work of Kochi (5) it is known that free cyclopropylmethyl radicals undergo fast ring opening even at temperatures as low as -100°.

If I reacts via mechanism b (not a) the secondary radical IV is an intermediate and this will undergo rapid ring fission, thus generating a *primary* radical V, which by addition to monomeric I leads to the nitroxide III with three β-hydrogens.



IV V

Assuming that photodissociation of the C-NO bond in I is not concerted with ring opening (6), it seems likely that nitroxide formation in general proceeds via the dissociation mechanism b.

Irradiations of I were carried out at 110° (thermal dissociation of dimer) with a mercury lamp (Philips SP 500 W) and a sodium lamp (Philips SON 400 W). Upon irradiation of I at room temperature with the mercury lamp (photochemical dissociation) the spectrum of III was also obtained.

The ESR spectra were recorded on a Varian E 3 spectrometer with an optical transmission cavity and a variable temperature accessory.

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