Nitroxides: Photochemical Synthesis of Trimethylisoquinuclidine *N*-Oxyl

By ANDRÉ RASSAT* and PAUL REY

(*Laboratoire de Chimie Organique Physique, Centre d'Etudes Nucléaires de Grenoble, Cedex No.* 85, *F.*38-*Grenoble-Gare, France*)

Summary The title compound has been prepared by photochemical denitrosation of 1,8-dinitroso-*p*-menthane.

STABLE nitroxides are generally prepared by oxidation of the corresponding amines or hydroxylamines,[1] or by organometallic coupling with nitro-compounds.[2]

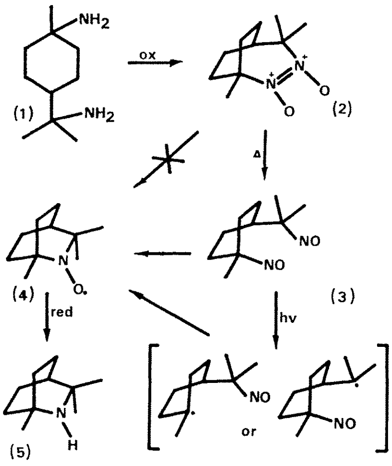
Radical addition to *C*-nitroso-derivatives,[3] although

$$R^1\cdot + R^2N{=}O \rightarrow R^1R^2N{-}O\cdot$$

effective in producing various nitroxides, has only been applied to the preparation of the stable caryophyllene iodonitrosite.[4]

We have investigated the possibility of photochemical denitrosation of a dinitroso-compound into a nitroso-alkyl radical giving a stable nitroxide by internal "spin trapping".

1,8-Diamino-*p*-menthane (1) (mixture of *cis*- and *trans*-isomers) is oxidized by *m*-chloroperbenzoic acid in methylene chloride[5] to a complex mixture, from which a crystalline product (m.p. 161°) is precipitated by diethyl ether [23% yield from the starting *cis–trans*-mixture of diamine (1)]. This colourless product turns blue on melting. Slightly



soluble in cyclohexane, it dissolves readily in boiling cyclohexane giving a blue solution, u v $\epsilon_{274} = 9750$,[6] n m r and microanalysis ($C_{10}H_{18}N_2O_2$) consistent with the azodioxy-structure (2)

When a boiling cyclohexane solution of (2) is irradiated with a 75 w (visible light) tungsten lamp, it gives an e s r signal whose intensity reaches a maximum after 1 h, the solution being orange-yellow By careful distillation of the solvent (azeotropic distillation with acetone), and chromatography on alumina, a red paramagnetic liquid (m p *ca* 4°) is obtained in 72% yield,† u v $\epsilon_{450} = 10{\cdot}4$, $\epsilon_{238} = 2480$, e s r (triplet of triplets $a_N = 17\ 40$ Oe, $a_H = 3\ 50$ Oe),‡ and mass spectra (*M* 168) are in agreement with structure (4) §

This radical can be reduced by lithium in liquid ammonia to the secondary amine (5) [u v , n m r data, and microanalysis of its picrate are consistent with the structure (5)]

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† Irradiation, under the same conditions, of a cold colourless methylene chloride solution of the diazoxy compound (2) leads to a quantitative recovery of the starting material

‡This e s r spectrum is identical with that observed from another azabicyclo[2 2,2]octane nitroxide obtained by independent synthesis [7]

§ Its globular structure makes this radical a potential spin label in plastic crystals

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