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PHOTOLYSIS OF THE STABLE NITROXIDE, 3-CARBAMOYL-2,2,5,5-TETRAMETHYLPYRROLINE-1-OXYL: A NEW PHOTOCYCLOELIMINATION OF NITRIC OXIDE

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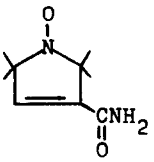
Stable nitroxide free radicals have recently come into prominence(1) particularly as spin-labeling molecules.(2,3) In order to assess the stability of the nitroxide moiety to ultraviolet irradiation, we have photolyzed three nitroxides, 1, 2 and 3. We report herewith our initial results.



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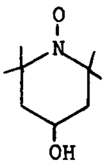

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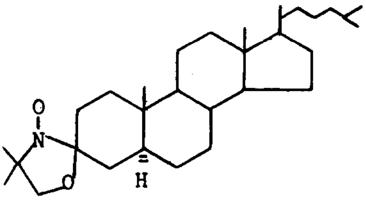

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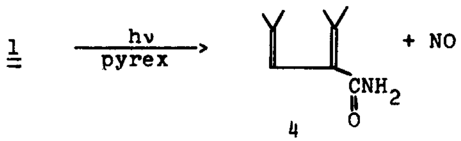
Irradiation(4) for 15 hr of a solution of 200 mg of 3-carbamoyl-2,2,5,5-tetramethylpyrroline-1-oxyl (1)(5,6) in 350 ml of purified benzene effected an approximate first-order decrease in esr signal intensity ($t_{1/2}$ = 2.0 hr) of aliquots removed at intervals during the reaction. Concentration of the benzene solution, filtration (see below), dilution with hexane and cooling afforded crystalline diene 4(7,8) which, when combined with diene 4 obtained from silica gel chromatography of the mother liquors, constituted a 95% yield, mp 79-84°. A small amount (< 4 mg) of impure starting nitroxide **1** was recovered from the chromatography, identified by its behavior by thin layer chromatography. A brown solid (decomp. 140-160°), slightly soluble in organic solvents, was obtained in 4% yield by filtration (see above) of the original benzene concentrate. This substance was not further investigated.



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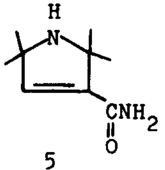

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Nitric oxide must have accompanied the formation of diene **4**, however, no attempt was made to isolate and identify this gas. The photocycloelimination of nitric oxide from **1** is a new cycloelimination reaction, analogous, for example, to the photocycloelimination of carbon monoxide from 3-cyclopentenone(10) and other unsaturated ketones(11) to form conjugated systems. The well known cycloelimination of sulfur dioxide from certain unsaturated cyclic sulfones(12,13) is an example of the thermal counterpart to these photoeliminations.

In contrast to nitroxide **1**, diene **4** and amine **5**(5,14) were completely stable to the photolytic conditions. Nitroxide **1** was stable thermally to at least 155° in boiling bromobenzene and exhibited no obvious decomposition below its melting point (204°) in the solid phase during a routine melting point determination.

Diene **4** probably results from excitation of one of the higher energy bands of nitroxide **1** which extends beyond 280 mμ. If this were not the case one might expect stable nitroxides in general to undergo ready photolytic reaction since many have maxima in the region of 420-460 mμ (ε 5-30). However, photolysis(4) of nitroxide **2**(15,16) and **3**(3,17) for 15 hr afforded the starting nitroxide in greater than 85% and 96% yield, respectively.(18)

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3. J. F. W. Keana, S. B. Keana and D. Beetham, J. Am. Chem. Soc., **89**, 3055 (1967).
4. Hanovia 200 watt high pressure mercury lamp with Pyrex filter.
5. E. G. Rozantzev and L. A. Krinitzkaya, Tetrahedron, **21**, 491 (1965).
6. $\lambda_{max}^{Dioxane}$ 211 (ϵ 14100); ϵ_{280} 400, ϵ_{300} 102, ϵ_{320} 75 and ϵ_{340} 63.
7. Found: C, 70.40%; H, 9.93%; N, 9.24%.
8. IR: $\nu_{max}^{CCl_4}$ 3500, 3180, 2940, 1675, 1600, 1450, 1380, 1360 cm^{-1}, UV: $\lambda_{max}^{Dioxane}$ 228 mμ (ϵ 11100), ϵ_{211} mμ, 11000; nmr: δ 5.8 (1 H, broadened singlet, vinyl proton), 5.8-7.2 (2 H, broad, amide protons) 1.61, 1.72, 2.05 (each, 3 H, doublet, J = 1 cps, three of the methyl groups), 1.83 (3 H, singlet, other methyl group); mass spectrum:(9) m/e 153 (parent ion), 138 (M - CH_3), 109 (M - $CONH_2$). The analytical speciman (white needles, hexane) had m.p. 86-87°.
9. We thank Professor D. A. Lightner, U.C.L.A. for the mass spectral determination.
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14. $\lambda_{max}^{Dioxane}$ 211 (ϵ 12000); ϵ_{280} 376, ϵ_{300} 79, ϵ_{320} 13, and ϵ_{340} 6.
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16. $\lambda_{max}^{Dioxane}$ 239 (ϵ 2000); ϵ_{280} 430, ϵ_{300} 71, ϵ_{320} 5, ϵ_{340} 2.
17. $\lambda_{max}^{Dioxane}$ 228 (ϵ 2300).
18. Nitroxide **2** and the corresponding ketone do undergo slow photodecomposition under our conditions ($t_{1/2} \approx 100$ hr) and we are investigating the nature of the products.