

The Photolysis of a 2-Methyl-1-Pyrroline 1-Oxide

By L. KAMINSKY and M. LAMCHEN

(Chemistry Dept., University of Cape Town, Rondebosch, Cape Town)

It has been established that irradiation of nitrones leads to the isomeric oxaziridines.¹ Todd and his co-workers have stated that whilst irradiation of 5,5-dimethyl-1-pyrroline 1-oxide (I; R¹=R²=Me, R³=R⁴=R⁵=H) produced the oxaziridine (II; R¹=R²=Me, R³=R⁴=R⁵=H), irradiation of 2-substituted-1-pyrroline 1-oxides, *e.g.* (I; R¹=R²=H, R³=R⁴=R⁵=Me) failed to yield oxaziridines.

We have, however, found that irradiation of 2,5,5-trimethyl-1-pyrroline 1-oxide (I; R¹=R²=R⁵=Me, R³=R⁴=H) gave a product in 28% yield

to which we have assigned the oxaziridine structure (II; R¹=R²=R⁵=Me, R³=R⁴=H) on the basis of the following data. Combustion analysis has shown the product to be isomeric with the starting nitron; the product showed no absorption between 210—320 m μ in the ultraviolet region and 1460—1800 cm.⁻¹ in the infrared spectrum, thus showing the absence of the nitron function, and in fact of any unsaturation. Two possible structures, the oxaziridine (II; R¹=R²=R⁵=Me, R³=R⁴=H) and the oxazetidine (III) could account for these results.

¹ M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, 1957, **22**, 576; J. Splitter and M. Calvin, *J. Org. Chem.*, 1958, **23**, 651; R. Bonnet, V. M. Clark, and Sir Alexander Todd, *J. Chem., Soc.* 1959, 2102.

The oxazetidine structure (III) was, however, excluded by nuclear magnetic resonance, since the spectrum (in deuteriochloroform) demonstrated the absence of a unique methine proton as required by the oxazetidine structure (III).

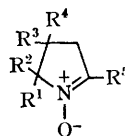
This spectrum also confirmed the oxaziridine structure (II; $R^1=R^2=R^5=Me$, $R^3=R^4=H$) since singlets were obtained at $\tau = 8.90$ (methyl group on C-5, *trans* to the oxaziridine ring), $\tau = 8.71$ (methyl group on C-5, *cis* to the oxaziridine ring) $\tau = 8.42$ (methyl group on C-2), and a complex multiplet from $\tau = 7.4-8.8$ (methylene protons on C-3 and C-4).

An active-oxygen determination showed the presence of 93% of the theoretically calculated oxygen content for the oxaziridine (II; $R^1=R^2=R^5=Me$, $R^3=R^4=H$).

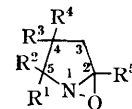
Deoxygenation of the nitron (I; $R^1=R^2=R^5=Me$, $R^3=R^4=H$) either with triphenylphosphine² or by reduction with zinc-acetic acid yielded 2,5,5-trimethyl-1-pyrroline (IV), b.p. 114°, ν_{max} 1655 cm^{-1} (C=N). Oxidation of the pyrroline (IV) with *m*-chloroperbenzoic acid, a reagent known to oxidise imines to oxaziridines,³ yielded a

compound which was shown by infrared spectroscopy and thin-layer chromatography to be the oxaziridine (II; $R^1=R^2=R^5=Me$, $R^3=R^4=H$).

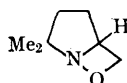
A further four products, in low yield, were obtained from the irradiation of nitron (I; $R^1=R^2=R^5=Me$, $R^3=R^4=H$).



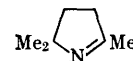
(I)



(II)



(III)



(IV)

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² F. Angolini and R. Bonnett, *Canad. J. Chem.*, 1962, **40**, 181.

³ A. Padwa, *Tetrahedron Letters*, 1964, 2001.