

## Stereoselective Photo-rearrangement of a Pyrroline 1-Oxide

By J. B. BAPAT and D. ST. C. BLACK

(Department of Chemistry, Monash University, Clayton, Victoria, Australia)

IRRADIATION of nitrones has been shown to form the isomeric oxaziridines.<sup>1</sup> Contrary to an earlier observation Kaminsky and Lamchen<sup>2</sup> reported that irradiation of 2,5,5-trimethyl-1-pyrroline 1-oxide (I; R<sup>1</sup> = R<sup>2</sup> = R<sup>5</sup> = Me, R<sup>3</sup> = R<sup>4</sup> = H) produced the oxaziridine (II; R<sup>1</sup> = R<sup>2</sup> = R<sup>5</sup> = Me, R<sup>3</sup> = R<sup>4</sup> = H) in 28% yield.

We have found that photolysis of 2,4-diphenyl-5,5-dimethyl-1-pyrroline 1-oxide (I; R<sup>1</sup> = R<sup>2</sup> = Me, R<sup>3</sup> = R<sup>5</sup> = Ph, R<sup>4</sup> = H) produced only one isomeric oxaziridine (II; R<sup>1</sup> = R<sup>2</sup> = Me, R<sup>3</sup> = R<sup>5</sup> = Ph, R<sup>4</sup> = H) (m.p. 155°) in 75% yield. Because of the unsymmetrical nature of the nitron, arising from the presence of the C-4 phenyl group, two isomeric oxaziridines (IIa and IIb) are possible.

Oxidation<sup>3</sup> of the related pyrroline<sup>4</sup> (III) with perbenzoic acid yielded a different product (m.p. 59°). An oxaziridine with a *cis*-arrangement of the C-2 and C-4 phenyl groups [*i.e.*, (IIb)] would be expected from the stereoselective nature<sup>5</sup> of the peracid oxidation. Thus, structure (IIa) (phenyl groups *trans*) was assigned to the photolysis product (m.p. 155°). Structures (IIa) and (IIb) were confirmed by the following evidence.

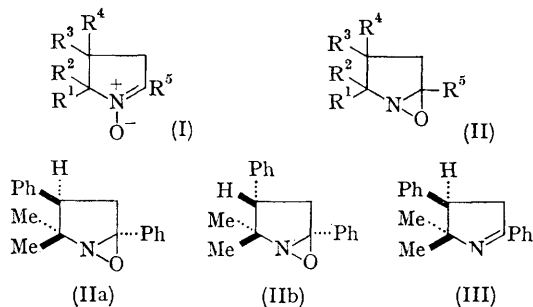
The formula C<sub>18</sub>H<sub>19</sub>NO was determined for both compounds by combustion analysis and molecular weight measurement [Found: *M* (osmometric in benzene), 230 (IIa); 242 (IIb). Calc.: *M*, 265]. Both products were active oxygen compounds and readily oxidised iodide ion to iodine. Ultraviolet

and infrared absorption spectra of (IIa) and (IIb) were compatible with these structures and were identical except for small differences in the infrared fingerprint region. The nuclear magnetic resonance spectra differed slightly as expected. In the spectrum of (IIa), the C-5 methyl groups appeared as singlets at  $\tau$  9.03 (*cis* to C-4 phenyl group and oxaziridine),  $\tau$  8.59 (*cis* to C-4 proton and C-2 phenyl group) and the remaining three ring protons (at C-3 and C-4) exhibited a complex ABC multiplet, from  $\tau$  6.6 to 7.0. The phenyl protons appeared as a complex multiplet from  $\tau$  2.3 to 2.8.

The nuclear magnetic resonance spectrum of (IIb) exhibited singlets at  $\tau$  9.18 (C-5 methyl group *cis* to C-4 and C-2 phenyl groups),  $\tau$  8.58 (C-5 methyl group *cis* to C-4 proton and oxaziridine), a complex ABC multiplet from  $\tau$  6.8—7.3 (C-3 and C-4 protons) and a complex multiplet from  $\tau$  2.3—2.8 (phenyl protons). A comparison of the methyl peaks of (IIa) and (IIb) is revealing. The peak at higher frequency (*i.e.*, shielded by C-4 phenyl group) should be lower in (IIa), because of a deshielding effect of the oxaziridine ring, whereas the lower-frequency peak (*i.e.*, *trans* to C-4 phenyl group) should be lower in (IIb), again because of

the deshielding effect of the oxaziridine ring. Both these effects are observed in the experimental values.

The two isomeric oxaziridines [(IIa) and (IIb)] can be interconverted *via* the nitron (I;  $R^1 = R^2 = \text{Me}$ ,  $R^3 = R^5 = \text{Ph}$ ,  $R^4 = \text{H}$ ) which is produced by acid-catalysed hydrolysis of each isomer, presumably by recyclisation of the initial  $\gamma$ -hydroxylamino-ketone;<sup>3</sup> this behaviour is characteristic of oxaziridines.<sup>3</sup>



(Received, November 21st, 1966; Com. 908.)

<sup>1</sup> M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, 1957, **22**, 576; J. S. Splitter and M. Calvin, *ibid.*, 1958, **23**, 651; R. Bonnett, V. M. Clark, and Sir Alexander Todd, *J. Chem. Soc.*, 1959, 2102.

<sup>2</sup> L. Kaminsky and M. Lamchen, *Chem. Comm.*, 1965, 130.

<sup>3</sup> W. D. Emmons, *J. Amer. Chem. Soc.*, 1957, **79**, 5739.

<sup>4</sup> J. B. Bapat and D. St. C. Black, *Chem. Comm.*, 1966, 902.

<sup>5</sup> B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1955, 1525.