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THE SYNTHESIS AND ELECTRON RESONANCE SPECTRUM OF THE NITROXIDE, 2,2,3,3-TETRAMETHYLAZIRIDINE-1-OXYL

Geoffrey R. Luckhurst and Franciska Sundholm*
Department of Chemistry, The University,
Southampton, SO9 5NH, England.

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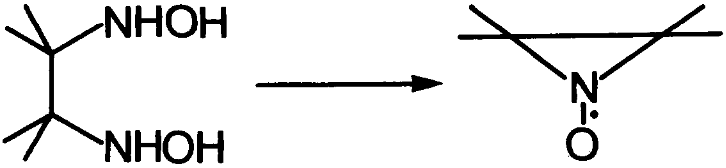
We have recently synthesised a series of nitronyl-nitroxides in order to study the anisotropic solute-solvent interaction when the radical is dissolved in a nematic mesophase.[1] One of the compounds used in the synthesis is 2,3-dihydroxylamino-dimethylbutane[2] (I) and, although hydroxylamines are said to be unstable,[3] we were still surprised to discover that, if left in the solid state, it is rapidly converted to a paramagnetic liquid. Colourless crystals (m.p. 58°-60°C) are formed on further standing; they are also intensely paramagnetic and appear to be quite stable. The radical formed is undoubtedly the three membered ring nitroxide 2,2,3,3-tetramethylaziridine-1-oxyl (II). We have yet to investigate the reaction mechanism, although the radical is probably produced by air oxidation of (I) to the corresponding nitroso compound[3] followed by photolytic cleavage, a reaction typical of nitroso compounds,[4] and finally ring closure.

(I)



(II)

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* Permanent address: Chemistry Department, University of Helsinki, E. Hesperiank. 4., Helsinki 10, Finland.

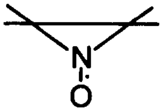
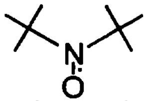
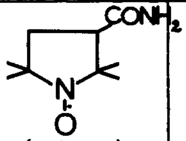
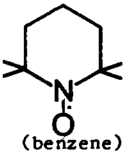
The product was purified for the electron resonance experiments by elution from an alumina column with toluene and for the mass spectrometry measurements by chromatography from a 10% polyethyleneglycol adipate/1% phosphoric acid column attached to the spectrometer. The VPC chromatogram of (I) after it had been left for four weeks contained five peaks with the last peak corresponding to 75% of the total recorded. The mass spectrum of the major component shows a maximum m/e peak at 114 with other peaks at m/e values of 99, 84, 69 and 54. This pattern is clearly in accord with structure (II), which should yield a peak at 114, while the other features are probably caused by ions formed by fragmentation through removal of the nitroso and methyl groups. The dominant product of the reaction is reduced, by refluxing with lithium aluminium hydride in ether for three hours, to give 2-amino-2,3-dimethylbutane (mass spectrum: m/e, 101, 98, 85, 59, 44, 43, 42). These results confirm the formation of 2,2,3,3-tetramethylaziridine-1-oxyl from (I).

The electron resonance spectrum of the paramagnetic product is also consistent with the nitroxide structure (II). The isotropic nitrogen-14 coupling constant is 40.6 MHz and the g-factor is 2.0058. Under higher gain several satellites are observed; one pair correspond to nitrogen-15 hyperfine structure with a coupling constant of 57.5 MHz. The ratio of the nitrogen couplings for the two isotopes is 1.42 in good agreement with that calculated from their magnetogyric ratios. The remaining satellites are caused by a carbon-13 splitting of 18.0 MHz and their intensities indicate that the coupling is to six equivalent carbon atoms. The nitroxide (II) clearly does not contain six equivalent carbon atoms, and so the four methyl carbons must have the same coupling constant as the two ring carbon atoms. A similar near degeneracy of carbon-13 splittings has been observed in perchlorodiphenylmethyl.[5] Finally, the largest component of the nitrogen-14 hyperfine tensor was determined from the electron resonance spectrum in a toluene glass at -120°C and is 94.9 MHz.

The electron resonance parameters for 2,2,3,3-tetramethylaziridine-1-oxyl are compared with those for other aliphatic nitroxides in the table. Often the hyperfine parameters can be invaluable in determining the detailed structure of a radical. We might have expected therefore, that the nitrogen coupling constants would have provided a guide to the arrangement of the atoms about the nitrogen nucleus. These expectations are not realised for the most striking feature of the parameters for the wide range of nitroxides, given in the table, is their great similarity. Indeed, the nitrogen splittings of these aliphatic nitroxides often exhibit a greater variation with the nature of the solvent than the size of

Table

The Magnetic Parameters for Various Aliphatic Nitroxides

Compound and solvent	$a\,^{14}\mathrm{N}$ (MHz)	$a\,^{15}\mathrm{N}$ (MHz)	$a\,^{13}\mathrm{C}$ (MHz)	$A_{\parallel}\,^{14}\mathrm{N}$ (MHz)	g-factor	Reference
 (toluene)	40.6	57.5	18.0	94.9	2.0058	This work
 (benzene)	43.2	60.6	12.0	94.9	2.0058	5,6
 (toluene)	39.9	54.7	25.8 14.3			This work
 (benzene)	43.2		16.0			7

the ring. The similarity of the nitrogen coupling constants does not necessarily mean that the hybridisation of the nitrogen orbitals is independent of the molecular geometry for molecular orbital calculations show how insensitive the coupling is to the state of hybridisation.[8] Accordingly we are unable to draw many conclusions concerning the structure of 2,2,3,3-tetramethylaziridine-1-oxyl from its coupling constants. The similar nitrogen coupling constants for the three and five membered ring nitroxides presumably indicates analogous configurations near the nitrogen atoms in both rings. The equivalence of the four methyl carbon-13 splittings might be taken to imply either planarity or rapid exchange between the non-planar configurations.

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