Tetrahedron Letters Vol. 21, pp 1557 - 1558
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0040-4039/80/0415-1557$02.00/0

AN UNUSUAL RESTRICTED ROTATION AROUND A REMOTE sp^2-sp^3 CARBON-CARBON BOND IN OXAZIRIDINES

Derek R. Boyd and Kenneth M. McCombe

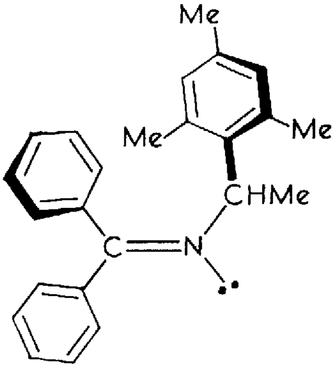
Department of Chemistry, The Queen's University of Belfast,
Belfast BT9 5AG, N. Ireland

and W. Brian Jennings

Department of Chemistry, University of Birmingham,
Birmingham B15 2TT, England

Summary: The barrier ($\Delta G^{\ddagger}$) to rotation about a remote aryl-CHMe bond shows a considerable increase upon oxidation of an imine to an oxaziridine.

There is considerable current interest in the stereochemistry[1-3] and the chemical reactivity[4] of oxaziridines bearing an α-hydrogen atom on the N-alkyl group.



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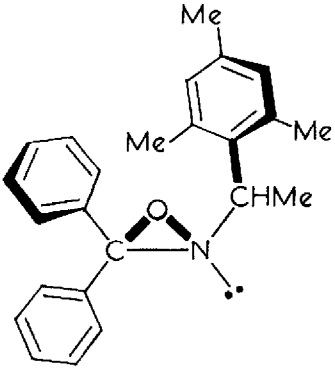

2

During the course of the latter investigations[4], compound 2 was synthesised[5] via the imine 1 and was found to have an abnormal ^{1}H NMR spectrum in $CDCl_3$ solution at ambient temperature. Thus two broad signals ($W_{\frac{1}{2}}$ 8Hz, each 3H), ascribed to markedly nonequivalent ortho-methyl groups in 2, were observed at δ 1.11 and 2.74. Furthermore, the mesityl meta-hydrogens were also anisochronous, giving rise to broadened signals (each 1H) at δ 6.57 and 6.82. Other features of the spectrum, mass spectral and microanalytical data were fully consistent with the proposed structure. The observed edge nonequivalence of the mesityl ring is assigned to an unusually high barrier to rotation about the mesityl-CHMe bond. In accord with this proposal the ortho-methyl signals and the meta-hydrogen signals broadened further on heating a sample in 1,1,2,2-tetrachlorethane solution and coalesced at 68.4° and 38.1°C respectively. The barrier to rotation ($\Delta G^{\ddagger}$) for the mesityl group was estimated to be 16.1 ± 0.3 and 15.8 ± 0.3 kcal mol^{-1}, at the respective coalescence temperatures of 68.4°

and 38.1°C, using the graphical procedure of Jaeschke *et al*[6] and the Eyring equation. Similarly the ambient temperature ^{13}C NMR spectrum in 1,1,2,2-tetrachlorethane also showed anisochronous *ortho*-methyl signals at δ 19.30 and 22.15 which coalesced at 39.5° corresponding to $\Delta G^{\ddagger} = 15.5 \pm 0.3$ kcal mol^{-1} in good agreement with the ^1H NMR data.

The imine 1 however, showed normal ^1H and ^{13}C NMR spectra at ambient temperature, though on cooling to -85° in CD_2Cl_2 solution the *ortho*-methyl groups were observed to become nonequivalent with signals at δ 1.51 and 2.77 in the ^1H spectrum and δ 20.42 and 22.37 in the ^{13}C spectrum. The barrier to rotation around the mesityl-CHMe bond in 1 was estimated to be $\Delta G^{\ddagger} = 10.4 \pm 0.3$ at -51.0° and 10.1 ± 0.3 kcal mol^{-1} at -68.0° from the ^1H and ^{13}C spectra respectively.

Clearly the cyclic oxygen atom in 2 brings about a remarkable increase in the barrier to rotation about the remote mesityl-CHMe bond, suggesting that the preferred conformations about the N-CHMe and mesityl-CHMe bonds are such that one *ortho*-methyl group interacts with this oxygen in the transition-state for rotation around the mesityl-CHMe bond. Additionally, the abnormally high field shift of one *ortho*-methyl signal in the ^1H NMR spectra of 2 and 1 (δ 1.11 and 1.51 respectively) as compared with the usual position of aryl-Me resonances (*ca.* δ 2.3) suggests that in the preferred ground-state conformation this methyl group lies close to the face of the *syn* C-phenyl ring.

The pentamethylphenyl analogues of 1 and 2 showed very similar effects in each case, though the barrier to rotation about the C_6Me_5-CHMe bond was slightly (*ca.* 0.5 kcal mol^{-1}) higher due to a buttressing effect on the *ortho*-methyl substituents.

Acknowledgments: We wish to thank Dr. R. Hamilton and Mr. N. May for assistance with the synthesis and NMR spectra respectively and the Northern Ireland Department of Education for a Postgraduate Studentship (to K.M.M.).

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(Received in UK 5 February 1980)