

INTRINSIC DIASTEREOTOPISM IN NORTRICYCLENE AND ADAMANTANE DERIVATIVES

D.G. Morris^{*} and A.M. Murray

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ,

and E.B. Mullock, R.M. Plews and J.E. Thorpe,

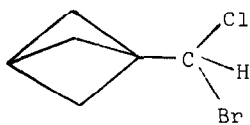
Research Division, Pfizer Limited, Sandwich, Kent.

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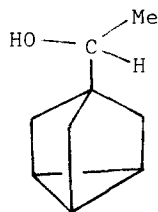
Intrinsic diastereotopism¹ of geminal protons may be exhibited by a molecule such as (I) where a three fold degenerate rotation axis around the C(1)-C(6) bond removes conformationally dependent effects. Two sub-classes have been recognised² and these have been given experimental basis in the apposite examples of Binsch³ and McKenna.⁴

We have demonstrated intrinsic diastereotopism for (i) the methylene protons of nortricyclenes in the presence of a chiral C(4) substituent and (ii) the β protons of adamantanes⁴ with a chiral bridgehead substituent.

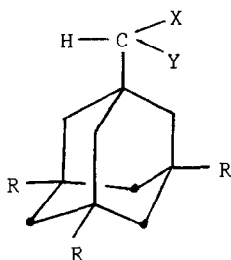
Nortricycene-4-carboxylic acid⁵ was converted to (II) via the methyl ketone by successive reaction with methyl lithium and lithium aluminium hydride. At 100 MHz (CDCl₃) the methylene protons of (II) gave a singlet; however in the presence of 0.4 molar equivalents of Eu(fod)₃ per mole of substrate the expanded spectrum showed an [AB]₃⁶ pattern for the methylene protons with $\Delta\nu = 52.9$ Hz and $J_{AB} = 10.0$ Hz. By comparison the methylene protons of a number of tri-cyclenes⁷ show $J_{gem} = 10.1-10.8$ Hz. In CS₂ solvent the methylene protons of (II) gave indications of an [AB]₃ pattern, but definitive assignments were prevented by overlapping with other absorptions. For the adamantane derivative (III) an [AB]₃ pattern, $\Delta\nu = 59.6$ Hz, $J_{AB} = 11.6$ Hz, was observed in the presence of 0.4 molar equivalents Eu(fod)₃. Also, addition of 0.3 molar equivalents Pr(dpm)₃ to (III) in CCl₄ caused an upfield shift of all resonances; for the β protons the [AB]₃ pattern gave $\Delta\nu = 10.8$ Hz, $J_{AB} = 12.2$ Hz. The values of J_{AB} for (IID, all ± 0.3 Hz, compare with a figure of 12.7 ± 0.4 Hz for the β -protons of IV.³



(I)



(II)



(III) R=H, X=Me, Y=OH

(IV) R=Me, X=Cl, Y=COR'

- ¹ K. Mislow and M. Raban, *Topics in Stereochemistry*, 1, 1, 1967.
- ² G.R. Franzen and G. Binsch, *J. Amer. Chem. Soc.*, 1973, 95, 175.
- ³ J. McKenna, J.M. McKenna and B.A. Wesby, *Chem. Comm.*, 1970, 867.
- ⁴ Nortricyclene (II) may be conceptually derived from adamantane (III) by deletion in the latter of the marked carbons and replacement by bridgehead-bridgehead bonds.
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We thank Professor Savers for additional experimental details.
- ⁶ C.W. Haigh, *J. Chem. Soc. (A)*, 1970, 1682.
- ⁷ S.A. Sherrod, R.G. Bergman, G.J. Gleicher and D.G. Morris, *J. Amer. Chem. Soc.*, 1972, 94, 4615.