

Stereochemistry of seven-membered heterocycles: XLIV. Spatial structure of 4-R-3,5-dioxabicyclo[5.1.0]octanes

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Abstract

4-R-3,5-Dioxabicyclo[5.1.0]octanes were prepared in good yields by reduction of the corresponding 8,8-dichloro derivatives in a system Li-t-BuOH. According to the data of dynamic ^1H and ^{13}C NMR spectroscopy involving experiments in the NOESY mode the formal (R = H) at -93°C in $(\text{CD}_3)_2\text{CO}$ exists in nearly equally occupied chair forms with endo- and exo-oriented three-membered ring. The like structure were found in the diastereomeric 4-Me(t-Bu)-analogs. The characteristic feature of ^{13}C NMR spectra consists in considerable difference in the chemical shifts of the C8 atoms ($\Delta\delta \sim 16\text{-}17$ ppm). The data on epimerization of diastereomers and calculations along AM1 procedure suggest for formal a three-component equilibrium including a twist-form. ©2005 Pleiades Publishing, Inc.

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