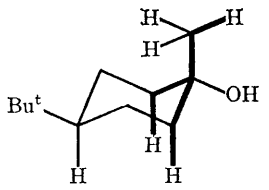
Line Widths of Nuclear Magnetic Resonance Signals due to Tertiary Methyl Groups

By C. W. SHOPPEE, F. P. JOHNSON, R. E. LACK, and S. STERNHELL
(*Department of Organic Chemistry, University of Sydney, Australia*)

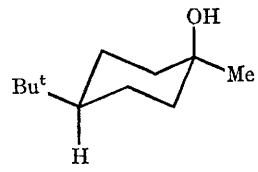
IN connection with our work on long range spin–spin coupling involving the angular methyl groups in steroids[1] we have examined in detail the n.m.r. spectra of *cis*-4-t-butyl-1-methylcyclohexanol (I), *trans*-4-t-butyl-1-methylcyclohexanol (II), their acetates, and the corresponding 2,2,6,6-tetradeuterated compounds.

The line widths at half height (W_H) of the signals due to *axial* methyl groups were in the range of 1·0—1·3 c./sec. and those due to *equatorial* methyl groups in the range of 0·6—0·7 c./sec. at a resolution at which the signals due to tetramethylsilane had W_H = 0·4—0·5 c./sec. In the deuterated derivatives both axial and equatorial methyl groups had W_H in the range of 0·5—0·6 c./sec. This result is in line with the extensive data observed in rigid systems[2] and, together with results from the steroid series[1,3] and decalins[4] indicates that line widths of n.m.r. signals due to tertiary methyl groups attached to undistorted six-membered rings could be used to determine their configuration and conformation, provided, of course, that the "favourable coupling paths"[2] [see heavy lines in formula (I)] terminate in protons.

The relationship does not hold for the geminal dimethyl group in α-pinene (both signals had W_H of 1·2—1·3 c./sec., as expected from models.



(I)



(II)

(*Received, June 25th*, 1965; *Com.* 396.)

[1] C. W. Shoppee, F. P. Johnson, R. E. Lack, and S. Sternhell, *Tetrahedron Letters*, 1964, 2319.
[2] M. Barfield, *J. Chem. Phys.*, 1964, **41**, 3825, and references cited therein.
[3] N. S. Bhacca, J. E. Gurst, and D. H. Williams, *J. Amer. Chem. Soc.*, 1965, **87**, 302.
[4] K. L. Williamson, private communication.