Steric Interference in Allylic and Pseudo-allylic Systems:[1] Magnitude of $A^{(1,3)}$ Methyl–Hydrogen Interactions and $A^{(1,3)}$ Methyl–Methyl Interaction

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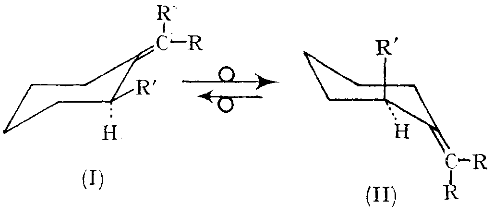
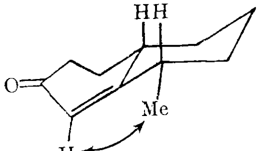
WE have recently pointed out[2] that in six-membered ring systems containing exocyclic double bonds as in (I) there exists a severe non-bonded steric interaction between the substituents R and R′, since the dihedral angle between them is ~0. This interaction was classified as $A^{(1,3)}$ strain and it was proposed that in mobile systems relief from this strain can be attained by conformational inversion to that conformer in which the sp^3 substituent becomes axial as in (II). In rigid systems R′ may attain this orientation by epimerization. We have now determined the approximate magnitude of $A^{(1,3)}$ strain in (I) when R = H and R′ = Me and when both R and R′ = Me.

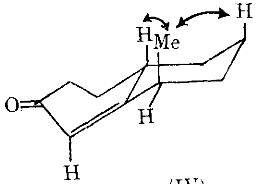


(I) (II)

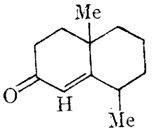
$A^{(1,3)}$ *Methyl–Hydrogen Interaction*: The equilibration of 8-methyl-$\Delta^{1(9)}$-octalin-2-one[3] with sodium methoxide in methanol gave a 2 : 1 mixture of epimers (III) and (IV).† Their stereochemical assignments were based on the n.m.r. spectrum of the mixture. It exhibited (in benzene) a broad singlet at 5·75 p.p.m. (vinylic, 1H), a doublet centred at 0·95 (*J* 7, 1H) and another doublet centred at 0·87 (*J* 6 c./sec., 2H). The latter doublet can be assigned to the equatorial C-8 methyl group in (III) and that at 0·95 p.p.m. to the axial methyl group in (IV), since (a) axial methyl groups appear at a lower field than the equatorial methyl groups and (b) the *J*-values for the former are larger than those for the latter.[4] Moreover the chemical shift of the C-8 methyl group in 8,10-dimethyl-$\Delta^{1(9)}$-octalin-2-one (V), in which this group is almost exclusively equatorial on steric grounds,‡ also occurs at 0·87 p.p.m. (benzene). Consideration of the two 1,3-diaxial methyl-hydrogen interactions (0·9 kcal./mole each) associated with (IV) and the free energy difference of 0·4 kcal./mole between the epimers in favour of (III) implies that $A^{(1,3)}$ methyl–hydrogen interaction [in (III)] is *ca.* 1·4 kcal./mole.



(III)

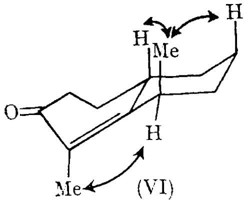


(IV)

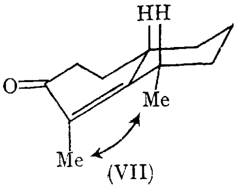


(V)

$A^{(1,3)}$ *Methyl–Methyl Interaction*: In order to determine the magnitude of this interaction 1,8-dimethyl-$\Delta^{1(9)}$-octalin-2-one was prepared by treating ethyl vinyl ketone with the pyrrolidine enamine of 2-methylcyclohexanone at reflux followed by acid hydrolysis. After treatment with sodium methoxide in methanol the product (b.p. 87—89°/1 mm.) was found to be homogenous by g.l.c. It exhibited in the n.m.r. spectrum (benzene solution) a doublet centred at 1·77 (*J* 2 c./sec., C-1 Me, 3H) and another doublet at 0·94 p.p.m. (*J* 7·2, C-8 Me, 3H) showing it to consist almost entirely of the C-8 axial epimer (VI).§ The corresponding C-8 equatorial epimer (VII) if present to the extent of 1–2% might have escaped detection. On taking into account one $A^{(1,3)}$ methyl–hydrogen interaction



(VI)



(VII)

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† Composition determined by g.l.c. with a column packed with 20% Carbowax on Chromosorb W.

‡ The C-8 axial methyl epimer suffers from a severe 1,3-diaxial Me–Me interaction.

§ The appearance of the C-1 methyl group as a doublet (*J* 2 c./sec.) is due to long range homo-allylic coupling with the C-10 proton. This signal would have appeared as a triplet or a doublet of doublets if an axial proton were present at the C-8 position; see J. T. Pinhey and S. Sternhell, *Tetrahedron Letters*, 1963, 275.

ca. 1·4 kcal./mole, and two 1,3-diaxial methyl–hydrogen interactions (0·9 kcal./mole each) associated with (VI) and the free energy difference of 2·7—3 kcal. between the two epimers in favour of (VI), we conclude that $A^{(1,3)}$ methyl–methyl interaction in VII) is about 5·9—6·2 kcal./mole.

Our values for these interactions are in a good agreement with those obtained by Allinger by machine calculations.[5]

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[3] G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, 1963, **85**, 207.

[4] F. Johnson, N. A. Starkovsky, and W. D. Gurowitz, *J. Amer. Chem. Soc.*, 1965, **87**, 3492.

[5] Personal communication.