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TORSIONAL EFFECTS IN BICYCLO[2, 2, 1]HEPTENES

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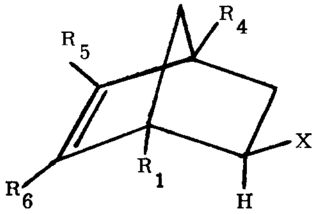
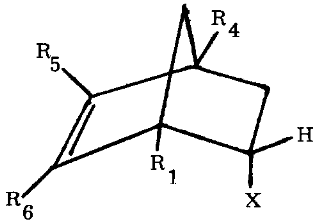
The exo selectivity in the reactions of various norbornyl derivatives has been explained by torsional effects which, it is alleged, destabilise the transition state leading to endo products.[1] However recent studies of the base catalysed deuterium exchange of substituted norbornanones have led Jindal and Tidwell[2] to conclude that 'torsional effects in such systems are either minor or are obscured by other factors'. We discuss here the results of equilibration studies of various bicyclo[2, 2, 1]heptenes which enable the relative magnitude of non-bonded interactions between C_1 and C_2 exo substituents and between C_1 and C_2 endo substituents to be observed and hence to permit an estimate of the importance of torsional effects.

The nitriles (1a - 1d and 2a - 2d) and the esters (1e - 1h and 2e - 2h) were isolated by preparative gas liquid chromatography of the reaction products of methylcyclopentadiene with acrylonitrile and with methyl acrylate respectively. Structures were assigned on the basis of spectral information and will be discussed elsewhere. The nitriles were equilibrated in t-butanol at 83° and the esters in methanol at 100°. In most cases equilibrium was approached from both sides (see Tables 1 and 2). The equilibration results show that with the exception of the pair of nitriles (1a and 2a) and of the pair of esters (1e and 2e) there is a negligible difference in free energy between epimeric pairs of exo and endo isomers. Although X-ray studies[3] indicate that the geometry of bicyclo[2, 2, 1]heptenes and bicyclo[2, 2, 1]heptanes can be distorted by substitution, the significant difference in energy of the nitriles (1a and 2a) and the esters (1e and 2e) must be attributed to non-bonded interactions. The dihedral angle between the C_1-methyl group and the <u>exo</u>-substituent is about 35° and that between the methyl group and the <u>endo</u>-substituent about 85°.[3] Our equilibration study implies a free energy difference of 0.39 kcal $mole^{-1}$ between 1a and 2a and a difference of 0.31 kcal $mole^{-1}$ between 1e and 2e. The 1,2-eclipsing interaction of methyl with cyano[4] (2.4 kcal $mole^{-1}$) is less than methyl with methoxycarbonyl[4] (4.5 kcal $mole^{-1}$). This suggests that the energy difference between the nitriles (1a) and (2a) is a better indication of non-bonded interaction between centrosymmetric groups than the difference between the esters (1e) and (2e), where conformational preferences of the methoxycarbonyl group may obscure the situation.[5]

1





2

a $R_1 = CH_3$; $X = CN$; $R_4 = R_5 = R_6 = H$

b $R_4 = CH_3$; $X = CN$; $R_1 = R_5 = R_6 = H$

c $R_5 = CH_3$; $X = CN$; $R_1 = R_4 = R_6 = H$

d $R_6 = CH_3$; $X = CN$; $R_1 = R_4 = R_5 = H$

e $R_1 = CH_3$; $X = CO_2Me$; $R_4 = R_5 = R_6 = H$

f $R_4 = CH_3$; $X = CO_2Me$; $R_1 = R_5 = R_6 = H$

g $R_5 = CH_3$; $X = CO_2Me$; $R_1 = R_4 = R_6 = H$

h $R_6 = CH_3$; $X = CO_2Me$; $R_1 = R_4 = R_5 = H$

i $X = CN$; $R_1 = R_4 = R_5 = R_6 = H$

TABLE 1

Equilibration of nitriles with potassium t-butoxide in t-butanol at 83° [a]

Starting Nitrile	% Endo product	% Exo product
1a	63.6	36.4
2a	63.6	36.4
1b	49.2	50.8
2b	49.2	50.8
2c	49.2	50.8
2d	51.6	48.4
2i	51	49

[a] see further ref. 6

TABLE 2

Equilibration of esters with sodium methoxide in methanol at 100° [a]

Starting ester	% Endo product	% Exo product
1e	60.3	39.7
2e	60.3	39.7
1f	50.2	49.8
2f	50.2	49.8
2g	49.9	50.1
2h	49.9	50.1

[a] see further ref. 5

Although the difference in energy between the nitriles (1a) and (2a) is small, these results establish the importance of torsional effects in determining the relative ground state energies of epimeric norbornenes. In previous studies it has not been possible to assign the contribution made by torsional effects to the difference in stability between exo and endo isomers. In the case of the nitriles (1a) and (2a) it is ~ 0.4 kcal mole^{-1}. If such effects are significant with a dihedral angle $\geqslant 35^{\circ}$, then in transition states with a dihedral angle $\sim 0^{\circ}$ a greater effect would be expected. This we hope to demonstrate by a kinetic study of the deuteration of the nitriles. Our results establish that 1-2 eclipsing interactions are a small factor contributing to the ground state stabilities of norbornenes and norbornanes.

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