

Evidence for a Preferred Conformation of the Bicyclo[3,3,2]decane System

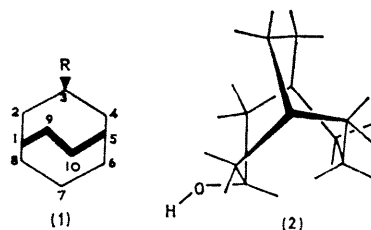
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DETAILS of the solvolytic behaviour of *exo*-3-bicyclo[3,3,2]-decyl toluene-*p*-sulphonate were required as part of an examination of transannular hydride shifts in bridged-ring systems¹⁻³ but although the epimeric bicyclo[3,3,2]decan-3-ols have been reported twice,⁴ no attempt had been made to assign configuration or preferred conformation.

The epimeric cyano-acetates, prepared from the cyano-hydrins of bicyclo[3,3,1]non-2-en-9-one, were reduced with lithium aluminium hydride to the corresponding amino-alcohols which were treated with nitrous acid to give a separable mixture of bicyclo[3,3,2]dec-2-en-9- and -10-ones. Subsequent Wolff-Kishner reduction produced bicyclo[3,3,2]dec-2-ene as a highly volatile, crystalline solid which, on hydroboration, was converted into two alcohols which were separated by preparative t.l.c. The ¹H n.m.r. spectrum of the more polar alcohol (m.p. 138—140°) revealed the carbinyl proton as a nine-line signal centred at τ 5.76 (J_{AX} 11 Hz, J_{BX} 5 Hz). The large coupling-constants are compatible with the carbinyl proton being axially disposed with respect to the cycloheptanol part of the molecule and the low-field position of this signal is due to the deshielding

by the *endo*-C(7) hydrogen atom.⁵ Hence the hydroxy-group in the more polar alcohol is *exo*-3 (i.e. 1; R = OH) and the preferred conformation must be as in (2).



Bicyclo[3,3,1]nonane is known to prefer a symmetrical, extended twin-chair conformation⁶ and we suggest that the conformation of the bicyclo[3,3,2]decane system although 'twin-chair' in form is in fact unsymmetrical (2) by virtue of having a staggered ethano-C(9)–C(10) bridge which reduces markedly the angle strain at C(9) and C(10) and also permits a greater flexing of the C(3) and C(7) methylene groups.

This configurational and conformational assignment is supported by the solvolytic behaviour of (1; R = O·SO₂·C₆H₄·Me-*p*), m.p. 88°—89°, in buffered acetic acid. The enhanced reactivity (Table) is ascribed to release of ground-state strain during ionisation as C(3) becomes *sp*³ hybridised and hence relieves the severe transannular C(3)—C(7) interaction.^{3,7} Similarly the large amount of olefin produced (94%) at the expense of *exo*- and *endo*-3-acetates (6%) reflects the fact that solvent capture of the 3-cation would re-establish this severe non-bonded interaction.

Acetolysis rate data

Toluene- <i>p</i> -sulphonate	<i>k</i> (sec. ⁻¹) (25°)	Relative rate
Cyclohexyl	4.88 × 10 ⁻⁸	1
Cycloheptyl	2.57 × 10 ⁻⁷	53
Cyclo-octyl	2.82 × 10 ⁻⁵	580
Bicyclo[3,3,1]non-3-yl ..	5.82 × 10 ⁻⁵	1200
Bicyclo[3,2,2]dec-3-yl ..	4.4 × 10 ⁻⁴	9000

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