The Mechanism of Hydrolysis of 2,3-*OO*-Benzylidene-norbornane-*exo*-2,-*exo*-3-diols

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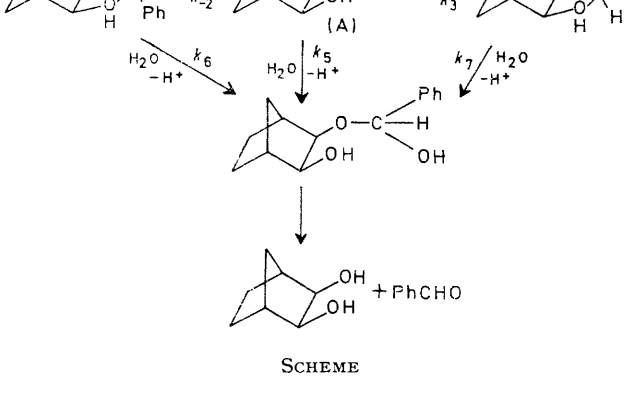
Summary The hydrolyses of the isomeric 2,3-*OO*-benzylidene-norbornane-*exo*-2,*exo*-3-diols occur at similar rates to their interconversion: interconversion of the corresponding *p*-methoxybenzylidene compounds is much faster than their hydrolysis and interconversion of the *p*-nitrobenzylidene compounds is slower than their hydrolysis; the hydrolyses may proceed through a bimolecular attack of water on the conjugate acid.

THE possibility that the carbonium ion formed by ring opening of the conjugate acid of a cyclic acetal in aqueous solution recyclises faster than it reacts with water has been considered several times[1] but there has been relatively little evidence for the occurrence of such a process.[2] It would be of interest to demonstrate this process since then formation of the carbonium ion could not be the rate-limiting step in the hydrolysis.

Norbornane-*exo*-2,*exo*-3-diol[3] forms two acetals with benzaldehyde which can be separated by thin-layer and column chromatography and which have different n.m.r. spectra. The most noticeable difference is that the signal of the benzylidene proton of one isomer [isomer (I)] occurs at 0·69 p.p.m. lower field than that of the other. Two acetals were also obtained from *p*-methoxybenzaldehyde and *p*-nitrobenzaldehyde and their n.m.r. spectra show similar differences.



SCHEME

Bagget and Foster and their co-workers[4] have shown that the signal of the benzylidene proton of the *trans*-isomer of 4-substituted and 4,5-disubstituted 2-phenyldioxolans is at 0·1 to 0·3 p.p.m. lower field than that of the *cis*-isomer. If the (larger) chemical shift difference found with the benzylidene norbornanediols is the result of similar configurational differences the configurations would be as shown in the Scheme. It is realised that this assignment may be

Extent of isomerisation accompanying hydrolysis of 2,3-OO-*benzylidene*-2,3-*norbornane*-exo-2,exo-3-*diols*

		Benzylidene (1M-HCl)			
		Isomer (I)		Isomer (II)	
Time (min)	Temperature (°)	% Hydrolysis[a]	% Other isomer[b]— ± 5%	% Hydrolysis[a]	% Other isomer[a]— ± 5%
5	22	30	30	30	6
10	23	35	45	45	9
20	23	70	61	70	17
		p-Methoxybenzylidene			
5[e]	22	12	80	12	13
2·5[f]	25	<1	53	<1	12
		p-Nitrobenzylidene (4M-$HClO_4$)			
40	25	23	13	—	—
90	25	44	17·5	—	—
10	25	—	—	35	<2
25	25	—	—	64	4

[a] Determined spectrophotometrically.
[b] Determined by n.m.r. spectroscopy.
[c] Defined as 100× (conc. of other isomer)/(total conc. of both isomers).
[d] In toluene the equilibrium mixtures contain 70 to 80% of isomer (II).
[e] 0·1 M-HCl.
[f] 0·01M-HCl.

incorrect as the conformation of the dioxolan ring in these compounds is probably different from that in the dioxolans studied by Baggett *et al.*,[4] but the following arguments do not depend on a knowledge of the correct configuration.

The hydrolyses of the benzylidenenorbornanediols in aqueous hydrochloric acid are accompanied by isomerisation as shown by the results in the Table. Isomerisation and hydrolysis of the unsubstituted compounds occur at roughly comparable rates but isomerisation of the *p*-methoxy-compounds is much faster than hydrolysis whereas isomerisation of the *p*-nitro-compounds is slower than hydrolysis. These results indicate that isomerisation has a more negative ρ-value than hydrolysis.

The mechanism of isomerisation is presumably that shown in the Scheme with ion (A) an intermediate. Hydrolysis could involve competitive capture of this ion by water (k_5) or nucleophilic attack by water on the conjugate acids (k_6 and k_7). If the former pathway is followed the initial rate constants for isomerisation and hydrolysis of isomer (I) are given by

$$\underset{\text{isom}}{k(\mathrm{I})} = k_{-3}k_2K_1/(k_{-2} + k_{-3} + k_5)$$

$$\underset{\text{hyd}}{k(\mathrm{I})} = k_5k_2K_1/(k_{-2} + k_{-3} + k_5)$$

so that $\underset{\text{isom}}{k(\mathrm{I})}/\underset{\text{hyd}}{k(\mathrm{I})} = k_{-3}/k_5$

The more negative ρ-value for isomerisation would therefore mean that the ρ-value for intramolecular attack by the hydroxyl group on the carbonium ion is more negative than for intermolecular attack by water. This seems unlikely. The alternative pathway for hydrolysis involving nucleophilic attack of water on the conjugate acid therefore seems the more probable as the smaller effect of substituents could be explained as a result of reduced carbonium ion character of the transition state.

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