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Acid-catalyzed Hydrolyses of Bridged Bi- and Tricyclic Compounds. XVII. Kinetics of Hydration and Rearrangement of 5-Methyl- and 2,5-Dimethyl-2-norbornenols and 5-Methylene- and 2-Methyl-5-methylene-2-norborneols

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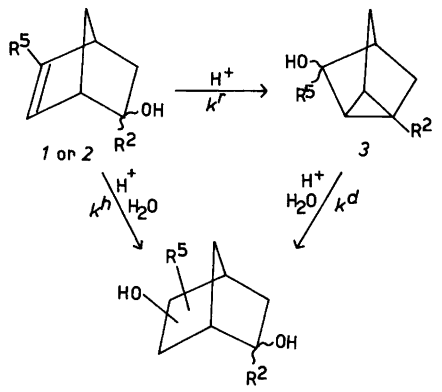
The effect of a 5-methyl group on hydration and rearrangement rates of *endo*- and *exo*-2-norbornenols (*1* and *2*, R^2 = H or Me, R^5 = Me) was studied. Reaction mechanisms were concluded mainly from solvent deuterium isotope effects to be *A*-S_E2 for the hydration of the 5,6-double bond (k_D/k_H 0.5 to 0.6) and *A*-1 for the homoallylic rearrangement of a substrate to the corresponding 3-nortricyclanol (*3*, k_D/k_H 2.7). A replacement of 5-hydrogen by methyl increases the hydration rate by a factor of 3×10^4 – 7×10^4 and the rearrangement rate by a factor of 60. For comparison hydration rates of 5-methylene-2-norborneols (*4* and *5*, R^2 = H or Me) were measured. They react from 6 to 16 times slower than the corresponding 5-methyl-2-norbornenols. The main reason is the difference in the initial state energies.



Scheme 1.

An aqueous mineral acid affects 2-norbornenols (*1* and *2*) in two different ways: it isomerizes them to 3-nortricyclanols (*3*; homoallylic rearrangement, k^r) and/or hydrates (k^h) them to norbornanediols (Scheme 1).[1,2] 3-Nortricyclanols are, however, intermediate products and are further hydrated (k^d) to norbornanediols. The extent of rearrangement and hydration depends on the position of the hydroxyl group (*exo* or *endo*) and on substituents. The *exo* alcohols (*2*) are rearranged more easily than the *endo* alcohols (*1*), *e.g.* in 1 mol dm^{-3} perchloric acid at 298 K the amount of rearrangement during the first three half-lives is *ca.* 8 % (possibly even smaller, see Ref. 3) for *endo*-2-norbornenol (*1*, R^2 = R^5 = H), *ca.* 16 % for *exo*-2- norbornenol (*2*, R^2 = R^5 = H), *ca.* 26 % for 2-methyl-*endo*-2-norbornenol (*1*, R^2 = Me, R^5 = H) and almost 100 % for 2-methyl-*exo*-2-norbornenol (*2*, R^2 = Me, R^5 = H). A 1-methyl group has a greater accelerating effect on rearrangement (by a factor of 4 – 10) than on hydration (1 – 4).[3]

A replacement of hydrogen by methyl at carbon 5 increases the rate of uncatalyzed solvolysis of 2-methyl-*exo*-2-norbornenyl *p*-nitrobenzoate in 80 % acetone-water at 298 K by a factor of 122 but has no effect on the rate of reaction for the *endo*-epimer.[4] The product formed from both epimers is 1,3-dimethyl-3-nortricyclanol (*3*, R^2 = R^5 = Me). These facts reflect a strong π-participation facilitated by 5-methyl group in the solvolysis of the *exo* ester.[4,5]

A methyl group at an ethylenic carbon has also a marked effect (10^3 to 10^6) on hydration rates of

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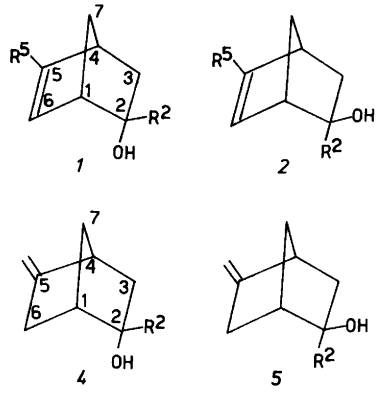


aliphatic alkenes and cycloalkenes if the neighboring ethylenic carbon is protonated, but only a slight effect (≤ 1) if protonation occurs at the methyl-substituted carbon.[6-8]

A replacement of hydrogen at carbon 5 by methyl in 2-norbornenols makes it possible to investigate the effect of 5-methyl on both rearrangement and hydration simultaneously. Therefore four 5-methyl-substituted 2-norbornenols [5-methyl-*endo*-2-norbornenol (*1*, $R^2 = H$, $R^5 = Me$), 5-methyl-*exo*-2-norbornenol (*2*, $R^2 = H$, $R^5 = Me$), 2,5-dimethyl-*endo*-2-norbornenol (*1*, $R^2 = R^5 = Me$) and 2,5-dimethyl-*exo*-2-norbornenol (*2*, $R^2 = R^5 = Me$)] were synthesized and their rates of disappearance and rearrangement were measured. For comparison the corresponding 5-methylene-2-norborneols [5-methylene-*endo*-2-norborneol (*4*, $R^2 = H$), 5-methylene-exo-2-norborneol (*5*, $R^2 = H$), 2-methyl-5-methylene-*endo*-2-norborneol (*4*, $R^2 = Me$) and 2-methyl-5-methylene-*exo*-2-norborneol (*5*, $R^2 = Me$)] were prepared and investigated, and equilibrium constants for isomerization 5-methyl-2-norbornenol $\overset{H^+}{\rightleftharpoons}$ 5-methylene-2-norborneol were measured.

EXPERIMENTAL

Syntheses. 5-Methyl-2-norbornenone was prepared from methylcyclopentadiene and 2-chloroacrylonitrile by the method of Goering and Chang.[9] A reduction of the ketone with lithium aluminum hydride in ethyl ether produced 5-methyl-*endo*-2-norbornenol (34 %) and 5-methylene-*endo*-2-norborneol (58 %) as main components. A reduction with aluminium-2-propoxide and 2-propanol[10] yielded a mixture of 5-methyl-*endo*-2-norbornenol (26 %), 5-methyl-*exo*-2-norborneol (39 %), 5-methylene-*exo*-2-norborneol (14 %) and 5-methylene-*endo*-2-norborneol (9 %). A treatment of the ketone with methyl magnesium iodide produced 49 % of 2,5-dimethyl-*endo*-2-norbornenol and 48 % of 2-methyl-5-methylene-*endo*-2-norborneol. A reaction with dimethyloxosulfonium methylide[11] and a reduction of the formed epoxides with lithium aluminium hydride yielded 15 % of 2,5-dimethyl-*endo*-2-norbornenol, 33 % of 2,5-dimethyl-*exo*-2-norbornenol, 7 % of 2-methyl-5-methylene-*exo*-2-norborneol and 44 % of 2-methyl-5-methylene-*endo*-2-norborneol. The components of the mixtures were separated on a preparative gas chromatograph using a Carbowax 20 M column.

A mixture of *cis*- and *trans*-1,3-dimethyl-3-nortricyclanols was prepared from 1-methyl-3-nortricyclanone[12] with methyl magnesium iodide. The isomers gave a single peak on GLC (Carbowax 20 M and FFAP columns).

The alcohols were identified from their IR, ^1H and ^{13}C NMR spectra,[13,14] except 2-methyl-5-methylene-*exo*-2-norborneol, which could not be isolated as pure. It was identified by GLC and kinetic data (see later).

Kinetics. Disappearance of substrates and formation of intermediate products were followed by GLC using FFAP and Carbowax 20 M columns, with cyclohexanone, norcamphor or camphor as inert internal standard. The disappearance of the bicyclic alcohols always obeyed fair first-order kinetics, with standard errors of the mean from 1 to 3 % (av. 2 %). A little isomerization of alcohols (especially of 5-methyl-2-norbornenols to 5-methylene-2-norborneols) and dehydration of norbornanediols to monoalcohols occurred in the gas chromatograph, which decreased the accuracy of measurements.

Equilibrations. Equilibrations between 5-methyl-2-norbornenols and 5-methylene-2-norborneols were carried out in aqueous perchloric acids (0.1 and 1.0 mol dm^{-3}) at room temperature (*ca.* 295 K) by starting with pure substrates. Samples were taken during several days. The isomeric pairs 5-methyl-*exo*-2-norbornenol $\rightleftharpoons$ 5-methylene-*exo*-2-norborneol and 2,5-dimethyl-*endo*-2-norbornenol $\rightleftharpoons$ 2-methyl-5-methylene-*endo*-2-norborneol gave fair equilibrium constants, but in the cases of 5-methyl-*endo*-2-norbornenol $\rightleftharpoons$ 5-methylene-*endo*-2-norborneol and 2,5-dimethyl-*exo*-2-norbornenol $\rightleftharpoons$ 2-methyl-5-methylene-*exo*-2-norborneol peaks of other isomeric alcohols disturbed the analyses so badly that no reliable results were obtained.

RESULTS

The disappearance rates of 5-methyl-2-norbornenols (*1* and *2*, $R^2 = H$ or Me, $R^5 = Me$) and 5-methylene-2-norborneols (*4* and *5*, $R^2 = H$ or Me)

Table 1a. Disappearance rate constants of 5-methyl-2-norbornenols (*1* and *2*) and 5-methylene-2-norbornenols (*4* and *5*) in aqueous perchloric acid.

Substrate	c_{HClO_4}/ mol dm^{-3}	T/K	$k_a \times 10^3$/ dm^3 mol^{-1} s^{-1}	Substrate	c_{HClO_4}/ mol dm^{-3}	T/K	$k_a \times 10^3$/ dm^3 mol^{-1} s^{-1}
1, R^2=H	0.100	283.2	2.14	*4*, R^2=H	0.100	293.2	1.14
R^5=Me	1.00	283.2	4.31		1.00	293.2	2.23
	0.100	293.2	7.89		(1.00	298.2	2.15)[a]
	0.104[c]	293.2	4.00		1.00	298.2	4.21[b]
	(1.00	298.2	13.0)[a]		0.100	303.2	3.81
	1.00	298.2	26.2[b]		0.104[c]	303.2	2.26
	0.100	303.2	21.0		0.100	313.2	14.2
	0.100	313.2	67.1		0.100	323.2	38.7
1, R^2=	0.100	283.2	1.80	*4*, R^2=Me	0.100	293.2	1.20
R^5=Me	1.00	283.2	4.19		1.00	293.2	2.19
	0.100	293.2	7.06		(1.00	298.2	2.24)[a]
	0.104[c]	293.2	3.57		1.00	298.2	4.09[b]
	(1.00	298.2	12.9)[a]		0.100	303.2	3.92
	1.00	298.2	30.0[b]		0.104[c]	303.2	2.30
	0.100	303.2	23.8		0.100	313.2	14.8
	0.100	313.2	73.5		0.100	323.2	42.1
2, R^2=H,	0.100	283.2	1.84	*5*, R^2=H	0.100	293.2	0.511
R^5=Me	1.00	283.2	4.77		1.00	293.2	0.998
	0.100	293.2	6.57		(1.00	298.2	0.977)[a]
	0.104[c]	293.2	3.53		1.00	298.2	1.91[b]
	(1.00	298.2	12.0)[a]		0.100	303.2	1.80
	1.00	298.2	31.1[b]		0.100	313.2	6.10
	0.100	303.2	22.2		0.104[c]	313.2	3.29
	0.100	313.2	63.9		0.100	323.2	16.7
2, R^2=	0.100	283.2	2.16	*5*, R^2=Me	0.100	293.2	0.619
R^5=Me	1.00	283.2	4.85		1.00	293.2	1.36
	0.100	293.2	7.99		(1.00	298.2	1.25)[a]
	0.104[c]	293.2	8.79		1.00	298.2	2.75[b]
	(1.00	298.2	15.1)[a]		0.100	303.2	2.53
	1.00	298.2	34.0[b]		0.100	313.2	7.81
	0.100	303.2	28.2		0.104[c]	313.2	4.19
	0.100	313.2	87.7		0.100	323.2	23.1

[a] Calculated from the activation parameters, not h_o corrected. [b] Calculated from the activation parameters, h_o corrected (see Results). [c] Deuterioperchloric acid.

Table 1b. Activation parameters (at 298.2 K) and solvent deuterium isotope effects.

Substrate	$\Delta G^{\neq}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$	k_D/k_H
No. R^2 R^5	kJ mol^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}	
1 H Me	83.78(10)	81(3)	−10(9)	0.507(19)
1 Me Me	83.82(3)	89(1)	16(3)	0.506(29)
2 H Me	83.98(3)	85(1)	3(3)	0.537(16)
2 Me Me	83.41(2)[a]	89(1)[a]	18(2)[a]	1.100(20)[a]
4 H	88.25(12)	91(3)	10(8)	0.593(30)
4 Me	88.14(11)	92(2)	13(8)	0.587(28)
5 H	90.20(8)	90(2)	−2(5)	0.539(15)
5 Me	89.60(12)	92(2)	8(8)	0.536(26)

[a] Apparent values owing to the two competing reactions, see Table 2.

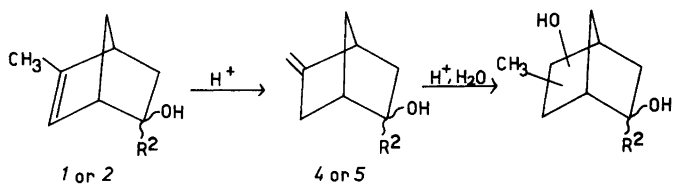
were measured in 0.100 mol dm^{-3} perchloric acid. The rate constants, activation parameters and solvent deuterium isotope effects are collected in Table 1. The activation parameters have been calculated from the second-order rate constants ($k_a = k_1/c_{HClO_4}$). The rate constants at 298.2 K calculated from the activation parameters are, however, not real rate constants in 1.00 mol dm^{-3} $HClO_4$, which was selected as a reference state for comparison of rates, since the second-order rate constants do not remain unchanged when the acid concentration varies between 0.1 and 1.0 mol dm^{-3}. Therefore one measurement per substrate was made in 1.00 mol dm^{-3} $HClO_4$ and the rate constants at 298.2 K calculated from the activation parameters have been corrected to the reference state by multiplying with the h_o correction factor: k_a (1.00 mol dm^{-3})/k_a (0.100 mol dm^{-3}) ($=2.3\pm0.3$ for *1* and *2* and 2.0 ± 0.2 for *4* and *5*).

Small GLC peaks of 5-methylene-2-norborneols were always observed in the hydrolyses of 5-methyl-2-norbornenols (7 to 16 %, as estimated with the method of consecutive reactions[15]). It is, however, difficult to conclude to what extent formation of the 5-methylene compounds occurred during the hydrolysis (Scheme 2) and how much of it was caused by decomposition of hydration products, norbornanediols, and isomerization of the substrates during the GLC analyses. Formation of 5-methyl-2-norbornenols in the hydrolyses of 5-methylene-2-norborneols was very slight or it could not be detected at all.

The product of homoallylic rearrangement of 5-methyl-*endo*- and -*exo*-2-norbornenols (*1*, and *2*, $R^2=H$, $R^5=Me$, Scheme 1) is 3-methyl-3-nortricyclanol (*3*, $R^2=H$, $R^5=Me$) and that of 2,5-dimethyl-*endo*- and *exo*-2-norbornenols (*1* and *2*, $R^2=R^5=Me$) is 1,3-dimethyl-3-nortricyclanol (*3*, $R^2=R^5=Me$, two isomers).[2,4,5] Only a very small GLC peak of 3-methyl-3-nortricyclanol was observed in the hydrolysis of 5-methyl-*exo*-2-norbornenol. Since the disappearance of 3-methyl-3-nortricyclanol occurs very slowly ($k_a^d = 4.8\times10^{-6}$ $dm^3\,mol^{-1}\,s^{-1}$, which is 6.5×10^3 times smaller than that of 5-methyl-*exo*-2-norbornenol in 1.00 mol dm^{-3} $HClO_4$ at 298.2 K),[1] the tiny peak shows that its formation cannot be significant. The peaks of the tricyclic alcohols were not observed at all in the hydrolyses of 5-methyl- and 2,5-dimethyl-*endo*-2-norbornenols. On the other hand, the formation 1,3-dimethyl-3-nortricyclanol was clearly observed in the hydrolysis of 2,5-dimethyl-*exo*-2-norbornenol. The formation rate of the tricyclic alcohol (k_a^r, Table 2) was estimated by the method of consecutive reactions.[15] Because of this the disappearance rates of a mixture of 1,3-dimethyl-3-nortricyclanols was measured (k_a^d, Table 2). The difference of the total disappearance rate of 2,5-dimethyl-*exo*-2-norbornenol (k_a), Table 1 and the formation rate (k_a^r) gives the hydration rate (k_a^h, Table 2) of the substrate. However, the last rate constant may include rates of other possible reactions of the substrate. Actually, several GLC peaks could be observed, but they were very small and did not change in the way typical of intermediate products.

In the following discussion the deductions will be drawn from the total disappearance rates in all cases except 2,5-dimethyl-*exo*-2-norbornenol, which evidently hydrolyzes *via* two competitive reaction paths: 23 % as rearrangement to 1,3-dimethyl-3-nortricyclanol and 77 % as hydration to norbornanediols in 1.00 mol dm^{-3} $HClO_4$ at 298.2 K (Table 2). The exclusion of other possible reactions of the substrates surely renders the kinetic data somewhat inaccurate, but the error is, in our opinion, not very significant. This can be seen in the reasonable values of kinetic isotope effects and relative rates (see Discussion).

The equilibration of 5-methyl-2-norbornenols and 5-methylene-2-norborneols gave at room temperature (*ca.* 295 K) the following equilibrium constants (K_c) and standard Gibbs energies ($\Delta G^\ominus = -RT\ln K_{c/c^\ominus}$): 5-methyl-*exo*-2-norbornenol $\rightleftharpoons$ 5-methylene-*exo*-2-norborneol, $K_c = 4.92\pm0.17$ and



Scheme 2.

Table 2. Rate constants of rearrangement to 1,3-dimethyl-3-nortricyclanol (k_a^r) and hydration (k_a^h) of 2,5-dimethyl-*exo*-2-norbornenol (*2*, $R^2=R^5=Me$) and disappearance rate constants (k_a^d) of a mixture of 1,3-dimethyl-3-nortricyclanols (*3*, $R^2=R^5=Me$) in aqueous perchloric acid, and activation parameters (at 298.2 K) and solvent deuterium isotope effects.

Substrate	c_{HClO4} / mol dm^{-3}	T/K	$k_a^r \times 10^3$ / dm^3 mol^{-1} s^{-1}	$k_a^h \times 10^3$ / dm^3 mol^{-1} s^{-1}	$k_a^d \times 10^3$ / dm^3 mol^{-1} s^{-1}
2, $R^2=$	0.100	283.2	0.512	1.65	
$R^5=Me$	1.00	283.2	1.12	3.73	
	0.100	293.2	1.89	6.10	
	0.104[a]	293.2	5.07	3.72	
	(1.00	298.2	3.61[b]	11.5)[b]	
	1.00	298.2	7.90[c]	26.1[c]	
	0.100	303.2	6.39	21.8	
	0.100	313.2	22.3	65.4	
3, $R^2=$	1.00	283.2			0.282
$R^5=Me$	1.00	288.2			0.613
	1.00	293.2			1.11
	1.00	298.1			2.31
	1.00	298.2			2.34[c]
	1.00	303.2			4.62
	0.100	303.2			2.39[d]
	0.104[a]	303.2			3.11[d]
$\Delta G^{\neq}$/kJ mol^{-1}			86.96(5)	84.09(4)	88.04(7)
$\Delta H^{\neq}$/kJ mol^{-1}			90(1)	88(1)	97(2)
$\Delta S^{\neq}$/J mol^{-1} K^{-1}			10(5)	14(3)	28(8)
k_D/k_H			2.68(25)	0.610(58)	1.30(7)

[a] Deuterioperchloric acid. [b] Calculated from the activation parameters, not h_o corrected. [c] Calculated from the activation parameters, h_o corrected (see Results). [d] The values of the rate constants decreased slightly towards the end of the run.

$\Delta G^{\ominus}$(298.2 K) = −3.95 ± 0.09 kJ mol^{-1}, and 2,5-dimethyl-*endo*-2-norbornenol ⇌ 2-methyl-5-methylene-*endo*-2-norborneol, K_c = 3.92 ± 0.28 and $\Delta G^{\ominus}$ (298.2 K) = −3.39 ± 0.18 kJ mol^{-1}.

DISCUSSION

The solvent deuterium isotope effects on the total disappearance rates of 5-methyl- and 2,5-dimethyl-2-norbornenols and 5-methylene- and 2-methyl-5-methylene-2-norborneols (k_D/k_H 0.51 to 0.59, Table 1) are typical of slow protonation of the carbon-carbon double bond by the $A-S_E2$ mechanism, an exception observed for 2,5-dimethyl-*exo*-2-norbornenol, when $k_D/k_H = 1.10$.[1-3,6,16] However, the isotope effect calculated in the last case for the difference of rates of total disappearance and rearrangement (0.61, Table 2) is in agreement with the $A-S_E2$ hydration. The isotope effects measured in this work for the hydration of methylenenorborneols (0.54 to 0.59) are normal and thus inverse to what (3.3) Paasivirta *et al.*[17] measured for the addition of formic acid to methylenenorbornane.

The deuterium isotope effect calculated for the rearrangement rate of 2,5-dimethyl-*exo*-2-norbornenol to 1,3-dimethyl-3-nortricyclanol (2.7, Table 2) is typical of the fast equilibrium protonation of the 2-hydroxyl group and of the subsequent rate-determining unimolecular elimination of a water molecule producing a carbocation (*A*-1 mechanism).[2] [The value measured for the disappearance of the 1,3-dimethyl-3-nortricyclanol mixture (1.3, Table 2) hints of rate-determining water addition to the pre-equilibrium protonated substrate (*A*-2 mechanism; *cf.* Ref. 18), but the value is approximate owing to the somewhat abnormal kinetics of the mixture of two isomers in 0.1 mol dm^{-3} $LClO_4$ (L = H or D) and requires checking.]

The activation entropies calculated for the total disappearance rates of the substrates (−10 to +20

J mol^{-1} K^{-1} at 298.2 K, Table 1) are partly more positive than values typical of slow protonation of the carbon–carbon double bond (≤ 0).[1,16,19] The abnormality is, however, so small, especially when the experimental scattering is taken into account, that it seems unnecessary to give it a special explanation. It may be due to side reactions (see Results).

The activation entropies calculated for the hydration and rearrangement of 2,5-dimethyl-*exo*-2-norbornenol (14 and 10 J mol^{-1} K^{-1}, respectively, Table 2) are equal within the limits of experimental error. This is not a reasonable result and is probably caused by experimental scattering, since usually the activation entropy of the *A*-1 mechanism is more positive than that of the $A-S_E2$ mechanism.[2] (The activation entropy is very sensitive to the experimental error and thus it is not as reliable an indication of the reaction mechanism as the solvent deuterium isotope effect.) The value 28 J mol^{-1} K^{-1} for the disappearance of 1,3-dimethyl-3-nortricyclanol is typical of the *A*-1 mechanism. This mechanism has been proposed for the hydrolysis of 3-methyl-3-nortricyclanol ($\Delta S^{\neq} = 34$ J mol^{-1} K^{-1}, $k_D/k_H = 2.1$).[1,20] [This comparison also makes the isotope effect (1.3) measured for the disappearance rate of 1,3-dimethyl-3-nortricyclanol doubtful (see above).]

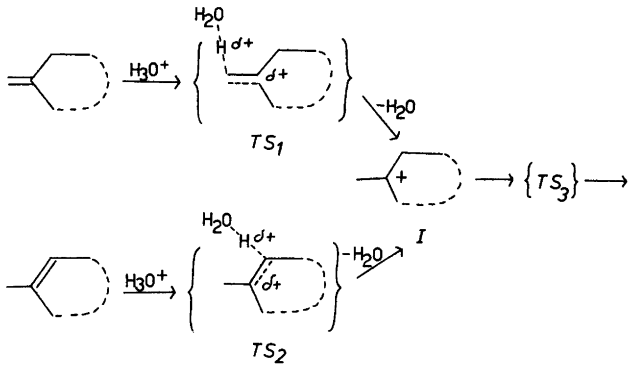
Based on the isotope effects (and activation parameters) it is probable that the disappearance of the substrates, with the exception of 2,5-dimethyl-*exo*-2-norbornenol, occurs totally or nearly totally *via* hydration of the 5,6-double bond by the $A-S_E2$ mechanism (k^h, Scheme 1). In the case of the exception mentioned, the *A*−1 rearrangement to 1,3-dimethyl-3-nortricyclanol (k^r, Scheme 1) competes with the hydration. Thus it is possible to compare the hydration rates of 5-methyl-2-norbornenols (*1* and *2*, R^2=H or Me, R^5=Me) with those of 2-norbornenols (*1* and *2*, R^2=H or Me, R^5=H)[1,2] and also with those of 5-methylene-2-norborneols (*4* and *5*, R^2=H or Me). Here the comparison is made with the h_o corrected rate constants in 1.00 mol dm^{-3} $HClO_4$ at 298.2 K calculated from the activation parameters (Tables 1 and 2).

A replacement of hydrogen at carbon 5 by methyl increases the protonation rate of 5,6-double bond by a factor of $3\times10^4-7\times10^4$ (the lower value is for the *endo*-2-norbornenols and the higher value for the *exo*-2-norbornenols),[1,2] The rate enhancements are very similar to that measured recently for the $A-S_E2$ hydration of 2-norbornenone (2×10^4).[16] They are also in agreement with that observed for the hydration of aliphatic alkenes (10^3 to 10^6) and cycloalkenes (*e.g.* 7×10^3).[6-8] This shows that the protonation occurs at carbon 6 (Markovnikov rule), and most probably from the *exo* direction, since the effect of the position (*exo* or *endo*) of the hydroxyl group and the nature of the 2-R-substituent (H or Me) upon the hydration rate is slight (see Tables 1 and 2). A similar small effect of the 2-methyl group has been observed earlier in the hydration of 2-norbornenols and 2-norbornenylmethanols.[1,2,21] However, the rate enchancing effect of the replacement of 2-hydroxyl by hydrogen has been observed to be marked (110–250, depending on the position of the hydroxyl group).[1,22] The observations agree better with the new inductive substituent constants (σ_I^q) by Grob *et al.*[23] than with the more classical ones (*e.g.* σ_I).[24]

The rate increasing effect of the 5-methyl group on the homoallylic rearrangement of 2-methyl-*exo*-2-norbornenol, 60,[2] is of the same order of magnitude as that observed by Brown *et al.*[4] in the uncatalyzed solvolysis of the corresponding *exo*-2-*p*-nitrobenzoates (122, see above).

Hydration of 5-methylene-2-norborneols (*4* and *5*) is 6 to 16 times slower than 5-methyl-2-norbornenols (*1* and *2*). A reason for the rate retardation might be found in the relative energies of the substrates. The equilibrium data in Results and the Gibbs energies of activation in Table 1 make the comparison possible. The initial state of 5-methyl-*exo*-2-norbornenol is 4.0 kJ mol^{-1} higher in energy than that of 5-methylene-*exo*-2-norborneol and the transition state of the hydration of 5-methyl-*exo*-2-norbornenol is 2.3 kJ mol^{-1} lower in energy than that of 5-methylene-*exo*-2-norborneol. Respectively, the initial state of 2,5-dimethyl-*endo*-2-norbornenol is 3.4 kJ mol^{-1} higher and the transition state 0.9 kJ mol^{-1} lower in energy than those of 2-methyl-5-methylene-*endo*-2-norborneol. This means that the main reason for the rate difference between the 5-methylene-2-norborneols and 5-methyl-2-norbornenols is the energy difference of the initial states.

The situation can be compared with another methylenecycloalkane – 1-methylcycloalkene pair, namely with methylenecyclobutane (*6*) and 1-methylcyclobutene (*7*), for which the equilibrium constant over a sodium-alumina catalyst $K(6\rightleftharpoons7)=5.66\pm0.16$ at 298 K and the ratio of hydration rates $k^h(6)/k^h(7)=2.6$ at 298 K (both the initial and transition states are in 0.972 mol dm^{-3} HNO_3; the rate ratio



Scheme 3.

is 5.8 when the initial states are in the gas phase and the transition states in the acid).[25,26] In this case the initial state of 1-methylcyclobutene is 4.3 kJ mol^{-1} lower in energy than that of methylenecyclobutane and the transition state of hydration of 1-methylcyclobutene is 2.0 kJ mol^{-1} lower in energy than that of methylenecyclobutane. Also in this case the main reason for the rate difference is the difference in the initial state energies. (The rate ratio, 5.8, when the initial states are in the gas phase, hints of even a smaller energy difference between the transition states, but the energy difference of the initial states is unknown.)

The transition states of hydration of 1-methylcycloalkenes and methylenecycloalkanes are in all the three cases quite similar in energy ($\Delta G^{\ominus}(Tss)$= 1 to 2 kJ mol^{-1}). The observed energy differences in this work are, however, larger than the experimental errors ($\lesssim$0.3 kJ mol^{-1}). This eliminates a hydration mechanism in which both isomers hydrate *via* a common transition state of the reaction (TS_3, Scheme 3), which should lie after a common cationic intermediate (*I*) in the reaction coordinate (*cf.* Refs. 17 and 27). Besides, this mechanism (*A*-1 or *A*-2) conflicts with solvent isotope effect, general acid catalysis and addition of only one deuterium atom per alkene molecule to the ethylenic carbons in deuterium oxide.[28-30] A more probable reason for the similar transition state energies is that the separate transition states (TS_1 and TS_2, Scheme 3) lie before the common intermediate (*I*; $A-S_E2$ mechanism), but so close to it that the transition states structurally resemble each other.[30] The small size of the transferring proton also makes steric hindrances slight in both cases. The situation of the transition states in the hydration reactions of bicyclic olefinic alcohols will be further studied in our laboratory.

REFERENCES

1. Lajunen, M. and Hirvonen, P. *Finn. Chem. Lett.* (1974) 245.
2. Lajunen, M. and Lyytikäinen, H. *Acta Chem. Scand. A 30* (1976) 63.
3. Lajunen, M. and Ollikka, R. *Finn. Chem. Lett.* (1978) 272.
4. Brown, H. C., Peters, E. N. and Ravindranathan, M. *J. Am. Chem. Soc. 97* (1975) 2900.
5. Brown, H. C., Ravindranathan, M. and Peters, E. N. *J. Am. Chem. Soc. 96* (1974) 7351.
6. Chwang, W. K., Nowlan, V. J. and Tidwell, T. T. *J. Am. Chem. Soc. 99* (1977) 7233.
7. Noyce, D. S. and Pollack, R. M. *J. Am. Chem. Soc. 91* (1969) 7158 and references therein.
8. Jensen, J. L. and Uaprasert, V. *J. Org. Chem. 41* (1976) 649.
9. Goering, H. L. and Chang, C.-S. *J. Org. Chem. 40* (1975) 2565.
10. Krieger, H. and Masar, S.-E. *Suom. Kemistil. 43* (1970) 318.
11. Bly, R. S., DuBose, C. M., Jr. and Konizer, G. B. *J. Org. Chem. 33* (1968) 2188
12. Paasivirta, J. *Ann. Acad. Sci. Fenn. A 116* (1962) 1.
13. Masar, S.-E. and Krieger, H. *Suom. Kemistil. 43* (1970) 315.
14. Lippmaa, E., Pehk, T., Paasivirta, J., Belikova, N. and Plate, A. *Org. Magn. Reson 2* (1970) 581.
15. Lajunen, M. *Acta Chem. Scand. A 28* (1974) 919.
16. Lajunen, M. and Sura, T. *Tetrahedron 34* (1978) 189.
17. Paasivirta, J., Kuorikoski, S.-L. and Laasonen, T. *Finn. Chem. Lett.* (1978) 42.

18. Lajunen, M. and Wiksten, P. *Finn. Chem. Lett.* (1980) 17.
19. Matesich, M. A. *J. Org. Chem. 32* (1967) 1258.
20. Lajunen, M. *Finn. Chem. Lett.* (1975) 153.
21. Lajunen, M. and Peuravuori, J. *Finn. Chem. Lett.* (1976) 99.
22. Lajunen, M. and Hirvonen, P. *Finn. Chem. Lett.* (1978) 38.
23. Grob, C. A., Schaub, B. and Schlageter, M. G. *Helv. Chim. Acta 63* (1980) 57.
24. Gordon, A. J. and Ford, R. A. *The Chemist's Companion*, Wiley, New York 1972, pp. 152–153.
25. Herling, J., Shabtai, J. and Gil-Av, E. *J. Am. Chem. Soc. 87* (1965) 4107.
26. Riesz, P., Taft, R. W., Jr. and Boyd, R. H. *J. Am. Chem. Soc. 79* (1957) 3724.
27. Paasivirta, J. *Acta Chem. Scand. 27* (1973) 374.
28. Williams, J. M. and Kreevoy, M. M. *Adv. Phys. Org. Chem. 6* (1968) 63.
29. Lajunen, M. and Wallin, M. *Finn. Chem. Lett.* (1974) 251.
30. Lajunen, M. and Wallin, M. *Finn. Chem. Lett.* (1975) 18.

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