Acid-Catalyzed Hydrolysis of Bridged Bi- and Tricyclic Compounds. 25. Comparison of the Hydrations of 2-Methyl-2-norbornene and 2-Methylenenorbornane with Those of 1-Methylcyclohexene and Methylenecyclohexane

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Hydration rates of 2-methyl-2-norbornene, 2-methylenenorbornane, 1-methylcyclohexene, and methylenecyclohexane were measured spectrophotometrically in aqueous perchloric acid. The activation parameters and solvent deuterium isotope effects are in all cases in agreement with the slow proton transfer to an olefinic carbon atom. The free energy diagrams show that the Gibbs energy of the transition state of protonation (hydration) is higher for methylenecycloalkanes than for methylcycloalkenes. The energy difference is small (0.8 kJ mol^{-1}) in the case of the bicyclic olefins and large (11.5 kJ mol^{-1}) in the case of the monocyclic olefins mentioned. Thus, no marked difference in the energies of the transition states caused by a possible distortion of the π-orbitals of 2-methyl-2-norbornene can be seen in the hydrations of the bicyclic olefins. An explanation for the latter large difference is evidently a change of conformation during the protonation of 1-methylcyclohexene, which possibly also causes an exceptionally low isotope effect (k_H/k_D = 1.13).

Recently a hypothesis of an unsymmetrical character of the π-orbitals of the carbon–carbon double bond in norbornene was presented.[1] It is supported by experimental data on the geometry of norbornene derivatives and by MO calculations (the olefinic hydrogen atoms are tilted 3–5° in the endo direction)[1a,2,3] (see, however, ref 4). It seems to account better for the great reaction rates and the exo–endo rate ratios found in the electrophilic additions to norbornene than the earlier hypotheses, e.g., steric hindrance of endo-5 and endo-6 hydrogens to the endo attack;[5] torsional strain effect,[6,7] release of the strain energy in the change of norbornene to the norbornyl cation,[8] and the low energy of the nonclassical norbornyl cation[9] (see, however, ref 10).

If one olefinic hydrogen of norbornene is substituted by a methyl group, a possible unsymmetrical character of the π-orbitals does probably not change markedly,[7] and thus the great reaction rate and the high exo–endo rate ratio should also prevail in the proton addition to 2-methyl-2-norbornene. But, what is the situation in the protonation of 2-methylenenorbornane, which produces the same 2-methyl-2-norbornyl cation as does 2-methyl-2-norbornene? The olefinic hydrogens are probably tilted slightly (0.1°) in the exo direction,[11] but it should not affect markedly the protonation rate. Thus, if the unsymmetrical character of the double bond is the reason for both the great protonation rates and the high exo/endo rate ratios in the case

Table I. Rate Constants of Hydration of 2-Methyl-2-norbornene (1), 2-Methylenenorbornane (2), 1-Methylcyclohexene (3), and Methylenecyclohexane (4) in Aqueous Perchloric Acid at Different Temperatures, Activation Parameters (at 298.2 K), and Solvent Deuterium Isotope Effects

substrate	c_{HClO_4}/ mol cm^{-3}	temp/K	$k_a/10^{-3}$ dm^3 mol^{-1} s^{-1}	activation parameters and solvent isotope effects
1	0.0104	278.2	40.4	k_H/k_D = 2.15 ± 0.13
	0.101	278.2	41.7	$\Delta G^{\ddagger}$ = 76.13 ± 0.07
	0.104	278.2	19.4[a]	kJ mol^{-1}
	0.0104	283.2	69.9	$\Delta S^{\ddagger}$ = −40 ± 6 J
	0.0104	288.2	115.5	mol^{-1} K^{-1}
	0.0104	293.2	186.2	$\Delta H^{\ddagger}$ = 64 ± 2 kJ
	0.0104	298.2	276	mol^{-1}
	1.00	298.2	658[b]	
2	0.101	278.2	1.383	k_H/k_D = 1.67 ± 0.12
	0.101	288.2	5.04	$\Delta G^{\ddagger}$ = 83.55 ± 0.10
	0.101	298.2	14.94	kJ mol^{-1}
	0.104	298.2	8.96[a]	$\Delta S^{\ddagger}$ = −24 ± 8 J
	1.00	298.2	28.7[b]	mol^{-1} K^{-1}
	0.101	308.2	38.4	$\Delta H^{\ddagger}$ = 76 ± 2 kJ
				mol^{-1}
3	1.00	288.2	0.178	k_H/k_D = 1.13 ± 0.09
	1.00	298.2	0.659	$\Delta G^{\ddagger}$ = 91.32 ± 0.07
	1.00	298.2	0.624[c]	kJ mol^{-1}
	1.07	298.2	0.582[a]	$\Delta S^{\ddagger}$ = −24 ± 6 J
	1.00	308.2	1.96	mol^{-1} K^{-1}
	1.00	318.2	5.49	$\Delta H^{\ddagger}$ = 84 ± 2 kJ
				mol^{-1}
4	1.00	288.2	0.412	k_H/k_D = 1.51 ± 0.08
	1.00	298.2	1.400	$\Delta G^{\ddagger}$ = 89.43 ± 0.08
	1.00	298.2	1.340[c]	kJ mol^{-1}
	1.07	298.2	0.926[a]	$\Delta S^{\ddagger}$ = −35 ± 6 J
	1.00	308.2	4.02	mol^{-1} K^{-1}
	1.00	318.2	10.14	$\Delta H^{\ddagger}$ = 79 ± 2 kJ
				mol^{-1}

[a] Measured in $DClO_4(D_2O)$. [b] Calculated from the activation parameters and corrected in regard to H_0 functions.[15] [c] Calculated from the activation parameters.

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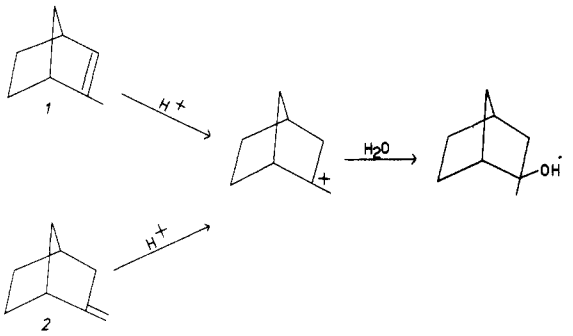
of norbornene and 2-methyl-2-norbornene, the kinetic data on the hydration of 2-methylenenorbornane should be different. This idea is investigated in the present work by employing 1-methylcyclohexene and methylenecyclohexane as reference compounds.

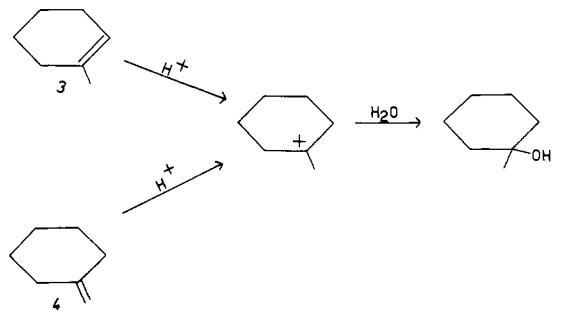
Results and Discussion

The hydration rates of 2-methyl-2-norbornene (**1**), 2-methylenenorbornane (**2**), 1-methylcyclohexene (**3**), and methylenecyclohexane (**4**) were measured in 0.01–1.00 mol dm^{-3} $HClO_4$ (or $DClO_4$) at different temperatures. The rate constants, activation parameters, and solvent deuterium isotope effects are listed in Table I. They all are typical of the rate-determining protonation of an olefinic carbon atom of the substrate, i.e., an A-S_E2 or Ad_E2 mechanism.[12,13] No inverted isotope effect observed by Paasivirta et al.[14] for the disappearance of 2-methylenenorbornane in formic acid–methylene chloride solution was found. The isotope effects of the bicyclic olefins in the present work are similar to those measured for 5-hydroxy-substituted 2-methyl-2-norbornenes and 2-methylenenorbornanes.[15] The hydration rate and isotope effect of 1-methylcyclohexene are very similar to those measured by Tidwell et al.[13] in sulfuric acid.

2-Methyl-2-norbornene and 2-methylenorbornane produce the common carbocation, 2-methyl-2-norbornyl ion, in protonation (eq 1) and the same alcohol, 2-methyl-*exo*-2-norborneol, in hydration (see Experimental Section).



Correspondingly, 1-methylcyclohexene and methylenecyclohexane produce the common intermediate 1-methyl-1-cyclohexyl cation and product 1-methyl-1-cyclohexanol in their hydration (eq 2; see Experimental Section). Thus, it is possible to compare the relative energies of the transition states in both cases if the initial state energies and the Gibbs energies of activation are known.



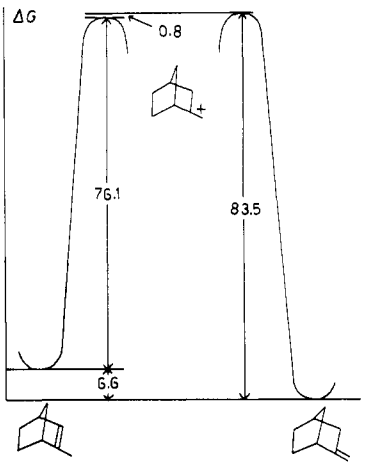


Figure 1. The Gibbs energy diagram of protonation (hydration) of 2-methyl-2-norbornene and 2-methylenenorbornane in dilute aqueous perchloric acid at 298.2 K (numerical values in kJ mol^{-1}).

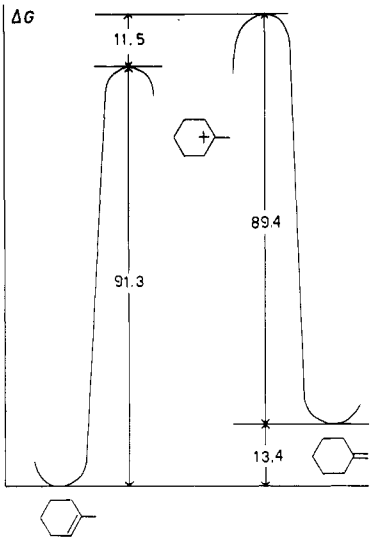


Figure 2. The Gibbs energy diagram of protonation (hydration) of 1-methylcyclohexene and methylenecyclohexane in 1.0 mol dm^{-3} aqueous perchloric acid at 298.2 K (numerical values in kJ mol^{-1}).

Equilibration of 2-methyl-2-norbornene (**1**) and 2-methylenenorbornane (**2**) gave the following values: $K(1 \rightleftharpoons 2) = 14.3 \pm 0.2$ (at ca. 293 K) and $\Delta G°(298.2\ K) = -6.59 \pm 0.04$ kJ mol^{-1} (see Experimental Section; cf. $\Delta G°(328.2\ K) = -6.66$ kJ mol^{-1} in *t*-BuOK–Me_2SO).[16] By assuming that the equilibrium constant (K) is the same in acetic acid and in dilute perchloric acid and by combining the free energy value with the activation Gibbs energies presented in Table I for **1** and **2** we get an energy diagram presented in Figure 1. According to it the energy of the transition state of protonation (hydration) for 2-methylenenorbornane is 0.83 ± 0.13 kJ mol^{-1} higher than that for 2-methyl-2-norbornene. The value is similar to those measured earlier for the hydrations of 2-methyl-*exo*-5-hydroxy-2-norbornene and 5-methylene-*exo*-2-norborneol (2.3 kJ mol^{-1}),[15] 2,5-dimethyl-*endo*-5-hydroxy-2-norbornene and 2-methyl-5-methylene-*endo*-2-norborneol (0.9 kJ mol^{-1}),[15] and 1-methylcyclobutene and methylenecyclobutane (2.0 kJ mol^{-1}).[17] The energy of the transition state of hydration for methylenecycloalkane is in all these cases

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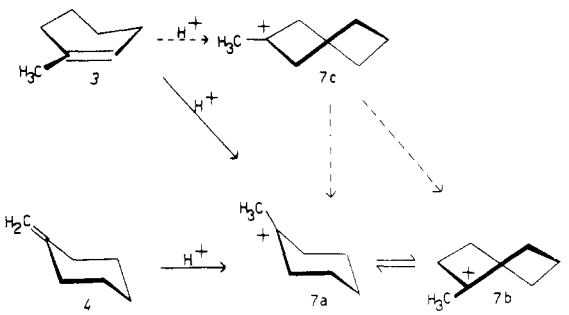
Scheme I



slightly (1–2 kJ mol^{-1}) higher than that for methylcycloalkene.

The equilibrium between 1-methylcyclohexene (**3**) and methylenecycloalkane (**4**) has been studied earlier under different conditions but with very similar results: $K(\mathbf{3} \rightleftharpoons \mathbf{4}) = 4.17 \times 10^{-3}$ to 5.05×10^{-3} and $\Delta G°(298.2\ \text{K}) = 13.35 \pm 0.24$ kJ mol^{-1}.[17,18] By combining the free energy value with the activation Gibbs energies of **3** and **4** in Table I we get an energy diagram presented in Figure 2. According to it the energy of the transition state of hydration for methylenecyclohexane is 11.5 ± 0.3 kJ mol^{-1} higher than that for 1-methylcyclohexene.

A possible explanation for this large difference is the difference of conformations of 1-methylcyclohexene (twist boat, **3**) and methylenecyclohexane (chair, **4**), which both produce the 1-methyl-1-cyclohexyl cation with a chair (**7a**) or twist-boat (**7b**) conformation (Scheme I).[19] If the change of conformation (from twist boat, **7c**) has already occurred at the (late) transition state of protonation of 1-methylcyclohexene, the result can be a marked decrease of energy (even 13.6 kJ mol^{-1})[19c] at the transitioin state.[19d] On the other hand, such a change of conformation is not needed in the protonation of methylenecyclohexane (Scheme I).

We can expect that the change of conformation should be indicated by some parameter which depends on the structures of the initial and transition states, e.g., the activation entropy or kinetic isotope effect. There are no clear differences in the activation entropies of the hydration of methylcycloalkenes and methylenecycloalkanes (Table I and ref 15), but the solvent deuterium isotope effect of 1-methylcyclohexene seems abnormally low ($k_H/k_D = 1.13$) as compared with those of many aliphatic or bicyclic olefins (≥1.5; this work and ref 13 and 15). However, the isotope effect is close to that measured for cyclohexene (1.06),[13] which also has a change of conformation in its protonation stage. Of course, the isotope effect can also be influenced by other factors, such as temperature, acid concentration, and hydration rate.[13,20]

There are no such changes of conformations in the protonations of 2-methyl-2-norbornene and 2-methylenenorbornane (or their 5-hydroxy-substituted derivatives)[15] as they have rigid structures. Thus, since their transition states are late, i.e., close to the common 2-methyl-2-norbornyl cation,[21] their energies should also be close to each other (the attacking proton is very small) unless there are other factors that have different effects on the energies of the transition states. Such a factor might be the unsymmetrical π-orbitals of 2-methyl-2-norbornene (see above), whose rate-increasing effect should take place at the transition state rather than at the initial state.[4] The energy difference between the transition states of protonation of 2-methyl-2-norbornene and 2-methylenenorbornane is, however, so small (0.8 kJ mol^{-1}) that it cannot alone explain the high reaction rates [k(2-methyl-2-norbornene)/k(1-methylcyclohexene) = 1054 in 1 mol dm^{-3} $HClO_4$ at 298 K] and great exo–endo rate ratios (ca. 170 in the protonation of 2-methyl-2-norbornene; see Experimental Section) in the hydration of norbornenes. Thus, the results of the present work, in agreement with our recent substituent effect data,[10] do not support the hypothesis[1] of the effect of a possible unsymmetrical character of the π-orbitals of norbornene upon the exceptional electrophilic addition reactions to the carbon–carbon double bond of norbornene.

Experimental Section

Syntheses. 2-Methyl-2-norbornene was produced as a mixture with 1-methyl-2-norbornene by the Diels–Alder reaction between methylcyclopentadiene and ethene.[22] The isomers were separated by a fractional distillation on a Perkin-Elmer 251 auto annular still. Their purities were higher than 99% (by GC).

2-Methylenenorbornane was prepared by application of the Wittig reaction between 2-norbornanone and phosphorane. The latter was obtained from methyltriphenylphosphonium iodide by the aid of potassium *tert*-butoxide in *tert*-butyl alcohol or *n*-butyllithium in absolute ether.[23] The former method gave a purer product (purity over 99%).

1-Methylcyclohexene was prepared by heating 1-methyl-1-cyclohexyl acetate[24] on potassium hydrogen sulfate and by redistillation of the olefinic product. Purity was 98.5%.

Methylenecyclohexane was a commercial product from Aldrich and was used without further purification. Its purity was over 99%.

The compounds were identified from their IR and ^{1}H and/or ^{13}C NMR spectra.[16,25]

Kinetic Measurements. The hydration rate constants of the substrates in aqueous perchloric acid were measured on a Cary 17 D spectrophotometer at a wavelength of 195 nm (without nitrogen atmosphere) after unsatisfactory efforts to measure them by GC (cf. ref 12). The initial substrate concentration was ca. 2×10^{-4} mol dm^{-3}. The first-order kinetics was always observed during two to three half-lives. The measurements were repeated at least once, often twice or more times.

Equilibration. 2-Methyl-2-norbornene (**1**) and 2-methylenenorbornane (**2**) were equilibrated in 100% acetic acid containing 0.2% of *p*-toluenesulfonic acid monohydrate as catalyst at room temperature.[18] A sample was added into aqueous potassium carbonate, and the alkaline solution was extracted with pentane. The pentane solution was analyzed on a Perkin-Elmer Sigma 2 B capillar gas chromatograph (XE 60 column). Both the pure initial olefins gave the same equilibrium mixture ([**2**]/[**1**] = 93.5:6.5; ±0.2), which also consisted of several other hydrocarbon peaks.

Product Analyses. Ca. 1 g of the substrate was shaken over 10 half-lives with 50 cm^3 of 1 mol dm^{-3} aqueous perchloric acid at appropriate temperature. The solution was extracted three

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times with CH_2Cl_2. The organic solution was dried on anhydrous K_2CO_3 and Na_2SO_4. The solvent was distilled off in low vacuum and the residue was analyzed by GC, IR, and ^{13}C NMR spectroscopy.[19b,25a] The only product was 2-methyl-*exo*-2-norborneol in the case of 2-methyl-2-norbornene and 2-methylenenorbornane and 1-methyl-1-cyclohexanol in the case of 1-methylcyclohexene and methylenecyclohexane.

Ca. 0.5 g of 2-methyl-2-norbornene was also hydrated in 25 cm^3 of 1 mol dm^{-3} $DClO_4(D_2O)$ at room temperature. The product was analyzed by GC, IR, and ^{13}C NMR (in CCl_4) and ^2H NMR (in CCl_4 with $CDCl_3$ as internal standard) spectroscopy (JEOL JNM-GX-400). The product was 3-deuterio-2-methyl-*exo*-2-norborneol, since the C-3 signal (48.1 ppm) split into a triplet in the C–H decoupled ^{13}C NMR spectra. A slight division of the C-2 signal (77.0 ppm) due to partial deuteration of the hydroxylic hydrogen was also observed. According to the ^2H NMR spectra, deuterium was mainly at the exo-3 position (99.4 ± 0.3%) and in minor quantity at the endo-3 position (0.6 ± 0.3%; the integrations were quite rough).

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(Trifluoromethyl)sulfonyl (Triflyl) Migration. Synthesis of 6,3′-Anhydro-3-benzyl-1-(5-chloro-5-deoxy-β-D-xylofuranosyl)barbituric Acid from the 2′-Trifluoromethanesulfonate (Triflate) of 6,5′-Anhydro-3-benzyl-1-β-D-ribofuranosylbarbituric Acid[1]

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The first evidence of (trifluoromethyl)sulfonyl (triflyl) migration is presented. The 2′,3′-*O*-stannylene derivative of 6,5′-anhydro-3-benzyl-1-β-D-ribofuranosylbarbituric acid (**1**) afforded a 9:1 mixture of isomeric 2′- and 3′-triflates **2** and **3** upon treatment with triflyl chloride in *N*,*N*-dimethylformamide. On acetylation, **2** and **3** afforded their corresponding acetyl derivatives **4** and **5**. Compound **4** was converted into 6,2′-anhydro-3-benzyl-1-(3-*O*-acetyl-5-chloro-5-deoxy-β-D-arabinofuranosyl)barbituric acid (**6**) by treatment with LiCl in hexamethylphosphoric triamide (HMPA), whereas **5** afforded the 6,3′-anhydro-xylo isomer **7**. Compounds **6** and **7** were reduced to the 5′-deoxy nucleosides **8** and **9**, respectively. Treatment of both 2′- and 3′-triflates **2** and **3** with LiCl in HMPA afforded, exclusively, the same 6,3′-anhydro-xylo derivative **10**, which was acetylated to **7**. The triflyl group on C-2′ in **2** migrated to C-3′ prior to the formation of the 6,3′-anhydro linkage during the conversion to **10**. A plausible mechanism is discussed.

During the past decade, the trifluoromethanesulfonate (triflate) group has become a useful and widespread reagent in synthetic organic chemistry[2] due to superior leaving ability and low nucleophilicity to conventional leaving groups such as mesylate, tosylate, or halide. We have been using the triflate leaving group extensively in nucleoside interconversion studies.[3-5] Recently, we found evidence for an unexpected (trifluoromethyl)sulfonyl (triflyl) migration. Since the triflyl group is commonly used in organic synthesis, our finding, as described below, should be taken into consideration in studies where a triflyl group neighboring an hydroxyl function is involved.

The 2′,3′-*O*-di-*n*-butylstannylene derivative of 6,5′-anhydro-3-benzyl-1-β-D-ribofuranosylbarbituric acid (**1**)[6] afforded a 9:1 mixture of isomeric 2′- and 3′-monotriflates **2** and **3** upon brief treatment with triflyl chloride in *N*,*N*-dimethylformamide (DMF). Compounds **2** and **3** were separated on a silica gel column. The ^1H NMR spectra (Table I) of both products show an AB quartet for H-5′,5″ and one exchangeable doublet, indicating the presence of the intact 6,5′-anhydro linkage and one secondary OH. A multiplet at δ 4.62 in the spectrum of the minor product is readily assigned to H-2′, as it collapsed to a sharp double doublet upon exchanging the dissociable proton with a deuterium, which coupled with H-1′ and H-3′ ($J_{1',2'}$ = 1.4 Hz, $J_{2',3'}$ = 5.8 Hz). These spectral data establish the minor

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(6) Compound **1** used in this investigation was prepared from 6,5′-anhydro-1-(2,3-*O*-isopropylidene-β-D-ribofuranosyl)barbituric acid [Otter, B. A.; Falco, E. A.; Fox, J. J. *J. Org. Chem.* **1969**, *34*, 1390] by benzylation with benzyl chloride in the presence of DBU followed by de-O-isopropylidenation with 80% trifluoroacetic acid. Deacetonation prior to benzylation was unsuccessful due to cleavage of the glycosyl bond. Benzylation of 6,5′-anhydro-1-β-D-ribofuranosylbarbituric acid [Lipkin, D.; Cori, C.; Sano, M. *Tetrahedron Lett.* **1968**, 5993. Maruyama, T.; Sato, S.; Honjo, M. *Chem. Pharm. Bull.* **1982**, *30*, 2688] was found to be less advantageous, since synthesis of their starting anhydro nucleoside is inefficient.

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