Acc. Chem. Res. 1985, 18, 254–258

Acid-Catalyzed Hydration of 5-Substituted Norbornenes

MARTTI LAJUNEN

Department of Chemistry and Biochemistry, University of Turku, SF-20500 Turku 50, Finland

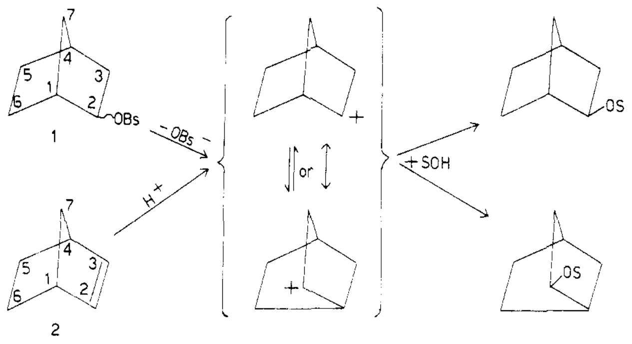
Received January 18, 1985 (Revised Manuscript Received May 31, 1985)

Investigations of bicyclo[2.2.1]heptyl or norbornyl cation and its formation and decomposition reactions have been extensive[1] ever since Winstein and Trifan[2] published their results on the solvolysis of *exo*- and *endo*-2-norbornyl *p*-bromobenzenesulfonates (brosylates, 1, Scheme I). They explained the exceptional kinetic and product-analytic results, e.g., the high exo/endo rate and product ratios, by formation of a bridged charge-delocalized symmetrical (nonclassical) carbocation. Its formation from the substrate occurs directly in the exo solvolysis and via a charge-localized (classical) cation in the endo solvolysis.

According to the theory of Brown,[1b–d] however, the high exo/endo rate and product ratios are due to steric hindrance of endo-6-hydrogen both to the departure of the endo leaving group and to the attack of a nucleophile from the endo direction. The rates of the corresponding exo reactions are normal, and thus no nonclassical ion is needed.

The structure of the norbornyl cation has lately been studied in super acids[1] and with advanced molecular orbital methods[3] and its energy of formation has been estimated,[4] but no full agreement about its character—whether it is nonclassical (one energy minimum) or rapidly equilibrating classical (two energy minima) or something else—has yet been reached.[1]

Scheme I



The norbornyl cation can also be formed from norbornene (2, Scheme I) via protonation of the double bond.[5] Typical of this reaction are the attack of a proton from the exo direction and an abnormally high reaction rate (e.g., $k_{\text{norbornene}}/k_{\text{cyclohexene}}$ = 600–23 000).[5m,o,p] This is characteristic not only of the proton attack but also of other electrophilic additions and cycloadditions to norbornene.[6] Several hypotheses have been proposed to explain these facts.

1. According to Brown[7] a reason for the high exo/endo rate ratio in the addition reactions to norbornene is the steric hindrance of endo-5- and endo-6 hydrogens to the endo attack. This explanation does not, however, seem very probable in the case of a proton attack although it can be more significant in the case of larger electrophiles.

2. Schleyer[8] has proposed that an increasing torsional strain between C-1–H and C-2–H may cause a decrease of rate of an endo attack to C-2. This effect is, however, probably small and can explain only part of the high rate ratio.[6b] Neither of the hypotheses above gives any explanation for the abnormally great rate of addition from the exo direction.

3. According to Huisgen[6b,9] the high ring strain of norbornene is partly released in the transition state of addition. Since the transition state of the protonation of norbornene better resembles the structure of norbornane than that of norbornene (see below), the difference between the ring strain energies of norbornene and norbornane (18–25 kJ mol^{-1})[5o,6b] is large enough to explain the high addition rates. However, the direct correlation between addition rates and ground-state energies does not seem general in the case of other cyclic

Martti Lajunen, docent of physical organic chemistry at the University of Turku, received his Ph.D. degree at the University of Turku in 1973 under the supervision of Professor Pentti Salomaa. His research activities are in hydrolytic reactions of bridged bi- and tricyclic compounds.

---

(1) E.g., reviews: (a) Barkhash, V. A. *Top. Curr. Chem.* **1984**, *116/117*, 1–265. (b) Brown, H. C. "Nonclassical Ion Problem" (with comments by P. v. R. Schleyer); Plenum Press: New York, 1977. (c) Brown, H. C. *Top. Curr. Chem.* **1979**, *80*, 1–18. (d) Brown, H. C. *Acc. Chem. Res.* **1983**, *16*, 432–440. (e) Grob, C. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 87–96. (f) Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426–431. (g) Olah, G. A. *Top. Curr. Chem.* **1979**, *80*, 19–88. (h) Olah, G. A.; Prakash, G. K. S.; Saunders, M. *Acc. Chem. Res.* **1983**, *16*, 440–448. (i) Sargent, G. D. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Wiley-Interscience: New York, 1972; Vol. 3, Chapter 24. (j) Walling, C. *Acc. Chem. Res.* **1983**, *16*, 448–454.

(2) Winstein, S.; Trifan, D. S. *J. Am. Chem. Soc.* **1949**, *71*, 2953; **1952**, *74*, 1147–1160.

(3) E.g.: (a) Goetz, D. W.; Schlegel, H. B.; Allen, L. C. *J. Am. Chem. Soc.* **1977**, *99*, 8118–8120. (b) Dewar, M. J. S.; Haddon, R. C.; Komornicki, A.; Rzepa, H. *Ibid.* **1977**, *99*, 377–385. (c) Wenke, G.; Lenoir, D. *Tetrahedron* **1979**, *35*, 489–498. (d) Köhler, H.-J.; Lischka, H. *J. Am. Chem. Soc.* **1979**, *101*, 3479–3486. (e) Yoshimine, M.; McLean, A. D.; Liu, B.; DeFrees, D. J.; Binkley, J. S. *Ibid.* **1983**, *105*, 6185–6186. (f) Raghavachari, K.; Haddon, R. C.; Schleyer, P. v. R.; Schaefer, H. F. III *Ibid.* **1983**, *105*, 5915–5917.

(4) E.g.: (a) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* **1978**, *100*, 5408–5416. (b) Arnett, E. M.; Pienta, N.; Petro, C. *Ibid.* **1980**, *102*, 398–400. (c) Arnett, E. M.; Hofelich, T. C. *Ibid.* **1983**, *105*, 2889–2895.

(5) E.g.: (a) Kwart, H.; Nyce, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 2601–2606. (b) Brown, H. C.; Liu, K.-T. *Ibid.* **1967**, *89*, 3898–3901. (c) Schleyer, P. v. R. *Ibid.* **1967**, *89*, 3901–3903. (d) Fry, A. J.; Farnham, W. B. *Tetrahedron Lett.* **1968**, 3345–3348. (e) Paasivirta, J. *Acta Chem. Scand.* **1968**, *22*, 2200–2214. (f) Brown, J. M.; McIvor, M. C. *J. Chem. Soc., Chem. Commun.* **1969**, 238–240. (g) Olah, G. A.; White, A. M.; DeMember, J. R.; Commeyras, A.; Lui, C. Y. *J. Am. Chem. Soc.* **1970**, *92*, 4627–4640. (h) Stille, J. K.; Hughes, R. D. *J. Org. Chem.* **1971**, *36*, 340–344. (i) Paasivirta, J. *Acta Chem. Scand.* **1973**, *27*, 374–376. (j) Kantolahti, E. *Ibid.* **1973**, *27*, 2667–2669. (k) Brown, H. C.; Liu, K.-T. *J. Am. Chem. Soc.* **1975**, *97*, 600–610; 2469–2476. (l) Brown, H. C.; Kawakami, J. H. *Ibid.* **1975**, *97*, 5521–5526. (m) Roberts, R. M. G. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1183–1190. (n) Qarroz, D.; Vogel, P. *Helv. Chim. Acta* **1979**, *62*, 335–360. (o) Chwang, W. K.; Nowlan, V. J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1977**, *99*, 7233–7238. (p) Allen, A. D.; Tidwell, T. T. *Ibid.* **1982**, *104*, 3145–3149.

(6) (a) Freeman, F. *Chem. Rev.* **1975**, *75*, 439–490. (b) Huisgen, R. *Pure Appl. Chem.* **1981**, *53*, 171–187.

(7) (a) Brown, H. C.; Hammar, W. J.; Kawakami, J. H.; Rothberg, I.; Vander Jagt, D. L. *J. Am. Chem. Soc.* **1967**, *89*, 6381–6382. (b) Brown, H. C.; Kawakami, J. H.; Liu, K.-T. *Ibid.* **1973**, *95*, 2209–2216.

(8) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 701–703.

(9) Huisgen, R. (a) *Proc. Chem. Soc.* **1961**, 357–369. (b) *Angew. Chem.* **1963**, *75*, 604–637.

0001-4842/85/0118-0254$01.50/0

Table I.
Total Disappearance Rates (k_{tot}), Protonation Rates of the Olefinic Carbons C-2 and C-3 (k_p), and Portions of Protonation of C-2 for 5-X-Substituted 2-Norbornenes in 1.00 mol dm^{-3} HClO$_4$ at 75 °C[14]

X	$\sigma_I{}^q$	k_{tot}/s^{-1}	k_p/s^{-1}	$k_p(C\text{-}2)/k_p$	ref
H	0	1.10×10^{-2}	1.10×10^{-2}	0.50	14d
H[a]		1.65×10^{-2}	8.3×10^{-3} [b]	0.50	14d
exo-CH$_2$OH	0.66	2.5×10^{-3}	2.5×10^{-3}	0.40	14b
endo-CH$_2$OH	0.66	2.3×10^{-3}	2.3×10^{-3}	0.40	14b
exo-CH$_2$Cl	1.02	1.48×10^{-3}	1.30×10^{-3}	0.35	14h
endo-CH$_2$Cl	1.02	6.7×10^{-4}	5.0×10^{-4}	0.35	14h
exo-COCH$_3$	1.69	1.05×10^{-3}	4.2×10^{-4}	0.40	14g
endo-COCH$_3$	1.69	1.07×10^{-3}	6.2×10^{-4}	0.40	14g
exo-OH	1.74	3.3×10^{-4}	2.7×10^{-4}	0.42	14a, 16c, 24
endo-OH	1.74	4.6×10^{-4}	4.1×10^{-4}	0.42	14a, 16c, 24
exo-CN	3.04	6.8×10^{-6}	6.8×10^{-6}	0.031,[c] 0.02[d]	14e, 23
endo-CN	3.04	6.1×10^{-6}	6.1×10^{-6}	0.021,[c] 0.02[d]	14e, 23
exo-NO$_2$	3.52	4.6×10^{-6}	4.6×10^{-6}	0.028	14f, i
endo-NO$_2$	3.52	2.0×10^{-5}	2.0×10^{-5}	0.028	14f, i
oxo	3.66[e]	4.4×10^{-7}	4.4×10^{-7}	0.40	14c

[a] 2,5-Norbornadiene. [b] Statistically corrected for two double bonds. [c] Measured kinetically in 1 mol dm^{-3} HClO$_4$ at 25 °C. [d] Measured from products in 5 mol dm^{-3} HClO$_4$ at 75 °C. [e] Calculated by means of a linear correlation between the substituent constants of Siegel and Komarmy and the $\sigma_I{}^q$ values.[27]

and bicyclic olefins[5o,6b] (see, however, ref 10). Besides, this hypothesis does not explain the high exo/endo rate and product ratios.

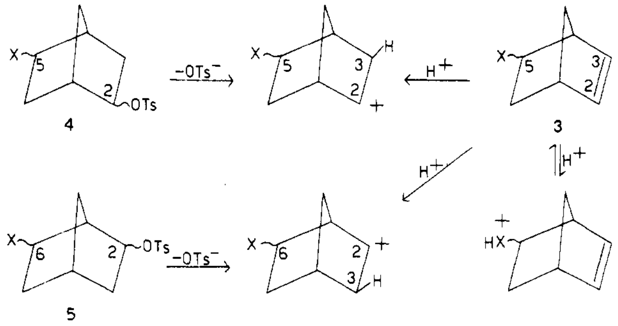
4. A possible explanation in the case of proton or another cation attack is the formation of a stable nonclassical cation.[5] According to product analyses the cation is, however, not symmetrical.[5] This fact is thought to accord better with the equilibrating classical cations. Besides, the nonclassical cation theory is not possible in additions or cycloadditions of uncharged electrophiles since no carbocation is formed.

5. The newest hypothesis offers the unsymmetrical π-orbitals of the double bond of norbornene; i.e., the exo lobe is larger and has higher electron density than the endo lobe, as an explanation for the easy formation of the exo transition state.[5o] This theory gives an explanation both for the high exo/endo rate ratio and for the high exo addition rate. MO calculations[11] and X-ray diffraction studies[12] suggest that the π-bond of norbornene is nonplanar and the olefinic hydrogens are tilted in the endo direction. Contradictory results have, however, been obtained.[13]

A generally accepted theory which would explain the high addition rates to norbornene and the high (?)[1] rates of solvolysis of exo norbornyl esters as well as the high exo/endo rate and product ratios in both these reactions is thus still lacking. Therefore investigations must be continued.

Grob[1e,f] has recently published results on the effect of 6-substituents (partly also 5- and 7-substituents) on the solvolysis rates and products of 2-norbornyl *p*-toluenesulfonates (tosylates). The results support strongly the formation of a bridged norbornyl cation. This cation is generally not symmetrical, contrary to the opinion proposed by Winstein (see above) but unsymmetrically bridged so that the amount of participation depends on the electron-releasing power of the substituent. This can be seen in the exo/endo rate and product ratios.

Scheme II



We have studied at the University of Turku during the last 10 years the acid-catalyzed hydration of norbornenes: kinetics and mechanism of the reaction and the effect of substituents on the reaction rates and products.[14] Protonation of 5-substituted 2-norbornenes **3** produces formally similar carbocations as the solvolyses of 5- and 6-substituted 2-norbornyl esters do (**4** and **5**, respectively, Scheme II; the cations are presented as classical, but they may as well be nonclassical). However, a proton can also attack the substituent itself, which side reaction must be eliminated. In addition, the protonation of the double bond must be divided between the olefinic carbon atoms C-2 and C-3.

Since the proton transfer from a hydronium ion to an olefinic carbon atom is probably the rate-determining stage of norbornene hydration (see below), as is general in the acid-catalyzed hydration of olefins,[5o,15] the formation of 5- and 6-substituted 2-norbornyl cations (or corresponding ion pairs) is the rate-limiting stage both in the hydration of the norbornenes and in the solvolyses of the norbornyl tosylates.[1] Therefore there should be correlations between the rates of these reactions. It would be of interest to study which of the solvolysis reactions of exo or endo tosylates resembles

---

(10) (a) Inoue, Y.; Ueoka, T.; Hakushi, T. *J. Chem. Soc., Chem. Commun.* **1982**, 1076–1077. (b) Inoue, Y.; Ueoka, T.; Kuroda, T.; Hakushi, T. *J. Chem. Soc., Perkin Trans. 2* **1983**, 983–988.

(11) E.g.: (a) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054–4061. (b) Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Mareda, J.; Mueller, P. H.; Houk, K. N. *Ibid.* **1982**, *104*, 4974–4976. (c) Spanget-Larsen, J.; Gleiter, R. *Tetrahedron* **1983**, *39*, 3345–3350.

(12) Pinkerton, A. A.; Schwarzenbach, D.; Birbaum, J.-L.; Carrupt, P.-A.; Schwager, L.; Vogel, P. *Helv. Chim. Acta* **1984**, *67*, 1136–1153.

(13) References 36 and 37 in ref 6b.

(14) (a) Lajunen, M.; Hirvonen, P. *Finn. Chem. Lett.* **1974**, 245–249. (b) Lajunen, M.; Peuravuori, J. *Ibid.* **1976**, 99–104. (c) Lajunen, M.; Sura, T. *Tetrahedron* **1978**, *34*, 189–192. (d) Lajunen, M.; Hirvonen, P. *Finn. Chem. Lett.* **1978**, 38–41. (e) Lajunen, M.; Sura, T. *Ibid.* **1979**, 233–235. (f) Lajunen, M.; Kukkonen, H. *Acta Chem. Scand., Ser. A* **1983**, *A37*, 447–451. (g) Lajunen, M.; Hintsanen, A. *Ibid.* **1983**, *37*, 545–552. (h) Lajunen, M. *Ibid.* **1985**, *39*, 85–91. (i) Lajunen, M., unpublished results.

(15) Nowlan, V. J.; Tidwell, T. T. *Acc. Chem. Res.* **1977**, *10*, 252–258.

more the hydration reaction. This knowledge may tell something about the characters of the transition states. For comparison, the total disappearance rates and the double-bond protonation rates of several *exo*- and *endo*-5-X-substituted 2-norbornenes (X = H, CH_2OH, CH_2Cl, $COCH_3$, OH, CN, NO_2, and =O or oxo)[14] measured by GC in 1.00 mol dm^{-3} $HClO_4$ at 75 °C are given in Table I.

The Mechanism of Hydration

The activation parameters, e.g., $\Delta S^{\ddagger}$, solvent deuterium isotope effects, and slopes of linear log k vs. H_0 correlations measured for the acid-catalyzed hydration of the double bond of the 5-X-substituted norbornenes are mostly typical of the rate-determining protonation of an olefinic carbon atom in aqueous mineral acid (A-S_E2 or Ad_E2 mechanism): $\Delta S^{\ddagger} \leq 0$ J mol^{-1} K^{-1}, $k_H/k_D \geq 1$, and slope ≈ -1.1.[14] A few somewhat exceptional values in the case when X = CH_2Cl or $COCH_3$ are probably due to the experimental scatter.[14g,h] The values above generally differ clearly from those measured for the side reactions which occur via initial pre-equilibrium protonation of the substituent (A-1 or A-2 mechanisms).[14g,h,16,17]

In some cases the occurrence of rate-determining proton transfer to an olefinic carbon was indicated by methods that prove more definively than the kinetic parameters above,[18] i.e., by general acid catalysis (X = OH, measured in phosphoric acid–dihydrogen phosphate buffers)[19] and by measurements of reaction rates in acidic H_2O–D_2O mixtures (X = OH or CH_2OH).[14b,20] A degree of proton transfer ($0 \leq \alpha \leq 1$) at the transition state of hydration of olefins can be estimated from these kinetic data.[18] α-Values between 0.6 and 0.9 (average 0.75 ± 0.05) were obtained for the norbornenes.[21] They refer to a late transition state; i.e., it lies close to the intermediate norbornyl cation. This interpretation is, however, not indisputable.[5o,22]

Portions of Protonation at C-2 and C-3

The protonation rate constants in Table I are the total protonation rates of the olefinic bond; i.e., they (k_p) are the sums of rate constants of protonation of C-2, k_p(C-2), and C-3, k_p(C-3), from the exo direction (the amount of endo protonation is evidently insignificant).[5,6] The division of the total constants into components was done in four ways: statistically (X = H), from product analyses (X = $COCH_3$, CN, or NO_2),[14f,g,i,23] from rate constants of hydration of 2- and 3-methyl-5-X-2-norbornenes (X = *endo*-OH, CN, or oxo),[14c,16,23,24] and by estimation from the values of other substrates (*exo*-OH, CH_2OH, or CH_2Cl).[14i] The results are not very accurate particularly in the cases where the portion of C-2 protonation is small.

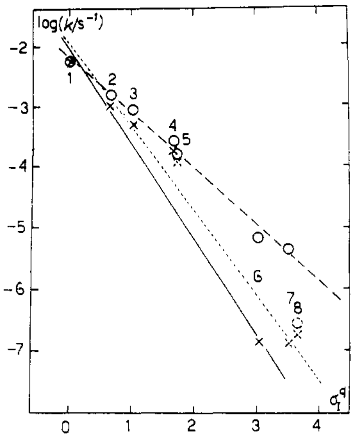


Figure 1. The logarithms of rate constants of protonation of the olefinic carbons of exo-5-substituted 2-norbornenes in 1.00 mol dm^{-3} $HClO_4$ at 75 °C vs. substituent constants $\sigma_I{}^q$. Symbols: ×, C-2 protonation; ○, C-3 protonation; 1, hydrogen; 2, hydroxymethyl; 3, chloromethyl; 4, acetyl; 5, hydroxyl; 6, cyano; 7, nitro; 8, oxo; - - -, C-2 protonation, all points included; —, C-2 protonation, part of points (×) excluded; – – –, C-3 protonation, part of points (○) excluded.

The amount of protonation at C-2, i.e., $k_p(\text{C-2})/k_p$, is presented in Table I for each substrate. It shows that the C-3 protonation is dominating. This can be expected, since the substituent at C-5 is generally more electron withdrawing than hydrogen and thus it destabilizes the generating positive charge at the closer carbon atom (due to C-2 protonation) more than at the more distant position (due to C-3 protonation) (see Scheme II). The large portion (40%) of protonation of C-2 in the case of 5-oxo-2-norbornene is exceptional but accords with an observed stabilizing effect of the oxo group at C-6 on the positive charge at C-2.[25]

Substituent Effects on the Protonation Rates

Before discussion of the effect of the 5-X-substituents on the protonation rates of the olefinic carbons, a possible influence of the acidic medium upon the substituents must be considered. If substituent X is protonated, its ability to withdraw electrons from the double bond is increased due to the positive charge and thus it retards electrophilic additions to the substrate more than the unprotonated substituent does.

Basicities of many X-substituted alkanes and cycloalkanes have been measured,[26] and these give estimates for the amount of protonation of substituent X in 5-X-2-norbornenes in 1 mol dm^{-3} $HClO_4$. The portion of the X-protonated substrate is ca. 1% (X = OH or CH_2OH) or less and has no significant effect on the rate of protonation of the double bond. It, however, causes side reactions (see above).

Because the incipient positive charge is rather far from the substituent in the protonation of 5-X-substituted 2-norbornenes at the olefinic carbon atoms, the protonation rates probably obey the inductive substituent constants (σ_I or $\sigma_I{}^q$),[27] according to eq 1, better

$$\log k_x = \rho\sigma + \log k_0 \qquad (1)$$

---

(16) (a) Lajunen, M.; Lyytikäinen, H. *Acta Chem. Scand., Ser. A* **1976**, *A30*, 63–68. (b) Lajunen, M.; Ollikka, R. *Finn. Chem. Lett.* **1978**, 272–275. (c) Lajunen, M.; Lyytikäinen, H. *Acta Chem. Scand., Ser. A* **1981**, *A35*, 131–138.

(17) Lajunen, M.; Tallgren, J. *Finn. Chem. Lett.* **1981**, 106–109.

(18) (a) Kresge, A. J. *Pure Appl. Chem.* **1964**, *8*, 243–258. (b) Williams, J. M.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1968**, *6*, 63–101. (c) Schowen, R. L. *Prog. Phys. Org. Chem.* **1972**, *9*, 275–332. (d) Bell, R. P. "The Proton in Chemistry", 2nd ed.; Chapman and Hall: London, 1973; Chapters 10–12.

(19) Lajunen, M.; Wallin, M. *Finn. Chem. Lett.* **1974**, 251–254.

(20) Lajunen, M.; Wallin, M. *Finn. Chem. Lett.* **1975**, 18–22.

(21) Lajunen, M.; Andersson, A. *Acta Chem. Scand., Ser. A* **1982**, *A36*, 371–376.

(22) (a) Johnson, C. D. *Tetrahedron* **1980**, *36*, 3461–3480. (b) Pross, A. *J. Org. Chem.* **1984**, *49*, 1811–1818.

(23) Lajunen, M.; Hiukka, R. *Acta Chem. Scand., Ser. A* **1985**, *A39*, 109–115.

(24) Lajunen, M.; Lyytikäinen, H. *Acta Chem. Scand., Ser. A* **1981**, *A35*, 139–143.

(25) Carrupt, P.-A.; Vogel, P. *Tetrahedron Lett.* **1982**, *23*, 2563–2566.

(26) (a) Arnett, E. M. *Prog. Phys. Org. Chem.* **1963**, *1*, 223–403. (b) Perdoncin, G.; Scorrano, G. *J. Am. Chem. Soc.* **1977**, *99*, 6983–6986.

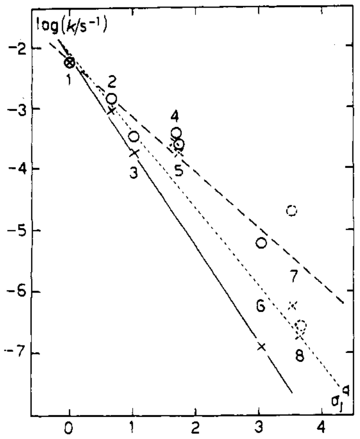


Figure 2. The logarithms of rate constants of protonation of the olefinic carbons of *endo*-5-substituted 2-norbornenes in 1.00 mol dm^{-3} $HClO_4$ at 75 °C vs. substituent constants $\sigma_I{}^q$. For a definition of the symbols, see Figure 1.

Table II.
Parameters of Eq 1 for the Protonation of C-2 and C-3 of 5-X-Substituted 2-Norbornenes in 1.00 mol dm^{-3} $HClO_4$ at 75 °C (r = Correlation Coefficient and n = Number of Points)

position of proton	position of X	n	$-\rho$	$-\log k_0$	$-r$	excluded points
C-2	exo	8	1.38	1.97	0.977	
C-2	exo	4	1.56	2.03	0.994	Ac,OH,NO_2, oxo[a]
C-2	endo	8	1.27	2.10	0.958	
C-2	endo	4	1.56	2.15	0.998	Ac,OH,NO_2, oxo[b]
C-3	exo	8	1.06	2.06	0.975	
C-3	exo	7	0.92	2.19	0.995	oxo
C-3	endo	8	0.96	2.19	0.931	
C-3	endo	6	0.92	2.24	0.968	NO_2, oxo

[a] The slope calculated for the excluded points = −1.57 (r = −0.996). [b] The slope calculated for the excluded points = −1.51 (r = −0.997).

than the direct resonance substituent constants. This was observed to be true in this case. The correlations of the protonation rate constants of C-2 and C-3 with the substituent constants $\sigma_I{}^q$ are presented in Figures 1 and 2 (the correlations are a little bit worse with σ_I). The plots are at least satisfactorily linear. Thus the inductive effects of the substituents are the dominating factors to determine the hydration rate. A marked scatter can, however, be seen in most of the plots. It is probably due to, besides the experimental inaccuracy, the fact that some substituents used have, in addition to their pure inductive effects, also other influences, i.e., frangomeric effects and neighboring group participation (X = OH, NO_2, oxo, or possibly $COCH_3$), which, however, are smaller in the hydration of norbornenes than in the solvolysis of 6-substituted 2-norbornyl sulfonates (**5**, Scheme II).[1e,f] These effects (together with field effects) are also probable reasons for the worse correlations of the endo-substituted norbornenes than of the exo ones.

The parameters of eq 1 and the correlation coefficients have been calculated for the C-2 and C-3 protonation of exo- and endo-substituted 2-norbornenes in Table II by employing both all eight points (that of 2,5-norbornadiene has been rejected) and selected points. In the latter case the points deviating markedly from the regression lines or representing substituents with frangomeric (C-2 protonation) or anchimeric effects were rejected. The points of the oxo substituent were also excluded since the protonation rate is evidently lower than expected in this case due to a homoconjugation between the carbon–carbon double bond and the oxo group in the initial state,[28] although a stabilizing effect of the oxo group on the positive charge can compensate this in the C-2 protonation.[25]

The correlations are generally good for the selected values (Figures 1 and 2 and Table II). It is surprising that also the slopes calculated only for the excluded points (Ac, OH, NO_2, and oxo; see footnotes of Table II) in the C-2 protonation are nearly equal with those calculated for the selected points (H, CH_2OH, CH_2Cl, and CN).

The slopes of the linear plots (reaction constants, ρ, or "inductivities", = $|\rho|$)[1e,f] of the exo and endo epimers are equal (Table II). They are a little (ca. 0.1) lower at 75 °C than at 25 °C.[14i] The higher inductivity of the C-2 protonation than that of the C-3 protonation is expected due to the closer distance between the generating charge and the substituent in the former case.

It is now possible to compare the inductivities of the norbornene protonation with those measured by Grob et al.[1e,f,29] for the solvolyses of 2-norbornyl tosylates in 80% ethanol–water at 70 °C. The comparison is possible since the same substituent constants were used in both investigations.

The inductivity of the C-2 protonation (ρ = −1.56) is smaller than those measured for the solvolyses of *exo*- and *endo*-6-X-*exo*-2-norbornyl tosylates (**5**-*exo*-OTs, ρ = −2.0 and −1.76, respectively)[1e,f] but greater than those measured for *exo*- and *endo*-6-X-*endo*-2-norbornyl tosylates (**5**-*endo*-OTs, ρ = −0.78 to −0.86 and −0.94 to −1.13, respectively).[1e,f,29] In these cases the formal positive charge is generated at C-2 and the substituent is at C-6 (Scheme II). The inductivity of the C-3 protonation (ρ = −0.92) is a little smaller than that measured for the solvolyses of *exo*-5-X-*exo*-2-norbornyl tosylates (**4**-*exo*-OTs, ρ = −0.96, which is similar to the value measured for *trans*-7-X-*exo*-2-norbornyl tosylates, ρ = −0.97),[29a,b] but clearly greater than that for *exo*-5-X-*endo*-2-norbornyl tosylates (**4**-*endo*-OTs, provided that it is close to the value measured for *trans*-7-X-*endo*-2-norbornyl tosylates, ρ = −0.72).[29a] In these cases the positive charge is generated at C-2 and the substituent is at C-5 (Scheme II). Thus the inductivity of the norbornene protonation is always between those measured for the solvolyses of the corresponding substituted *exo*- and *endo*-2-norbornyl tosylates. The medium has, however, some effect on the reaction constant.[29a] A more concise comparison (X = H or CN) with similar conclusions can also be done with the solvolysis data by Apeloig et al.[30] and by Wilcox and Tuszynski.[31]

---

(27) (a) Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119–251. (b) Grob, C. A.; Schaub, B.; Schlageter, M. G. *Helv. Chim. Acta* **1980**, *63*, 57–62. (c) Siegel, S.; Komarmy, J. M. *J. Am. Chem. Soc.* **1960**, *82*, 2547–2553.

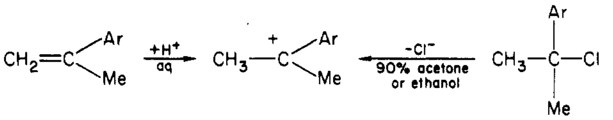
(28) (a) Lajunen, M.; Ihantola, A.; Tallgren, J. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 365–369. (b) Werstiuk, N. H.; Taillefer, R.; Bell, R. A.; Sayer, B. *Can. J. Chem.* **1973**, *51*, 3010–3014.

(29) (a) Bielmann, R.; Christen, M.; Flury, P.; Grob, C. A. *Helv. Chim. Acta* **1983**, *66*, 2154–2164. (b) Grob, C. A.; Sawlewicz, P. *Tetrahedron Lett.* **1984**, *25*, 2973–2976. (c) Fischer, W.; Grob, C. A.; von Sprecher, G.; Waldner, A. *Ibid.* **1979**, *21*, 1901–1904. (d) Grob, C. A.; Günther, B.; Hanreich, R.; Waldner, A. *Ibid.* **1981**, *22*, 835–838.

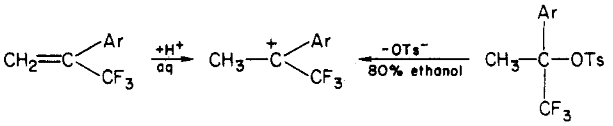
(30) Apeloig, Y.; Arad, D.; Lenoir, D.; Schleyer, P. v. R. *Tetrahedron Lett.* **1981**, *22*, 879–882.

(31) Wilcox, C. F., Jr.; Tuszynski, W. J. *Tetrahedron Lett.* **1982**, *23*, 3119–3122.

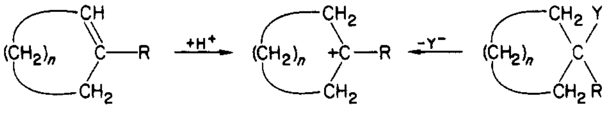
The following comparisons between the reaction constants of solvolysis and hydration reactions which produce the same carbocations or oxocarbocations show that the absolute value of the reaction constant is generally higher in the solvolysis (eq 2–5).[32] An explanation might be an earlier transition state of protonation; i.e., there is less carbocation character in the transition state of protonation than in that of solvolysis. The carbocation character is probably very largely developed in the solvolysis transition state (89%?).[33] Thus the α-value (0.75, see above) measured for the protonation of norbornenes seems to be at least qualitatively right.


(2)

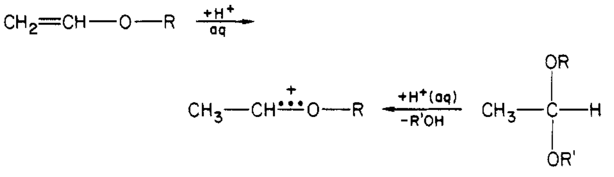
$\rho^+(\mathrm{RCl}) = 1.6\ \rho^+(\mathrm{olefin})$[32a]


(3)

$\rho^+(\mathrm{ROTs}) = 1.9\ \rho^+(\mathrm{olefin})$[32a]


(4)

$\log k_n(\mathrm{RY}) \approx 2.2 \log k_n(\mathrm{olefin}) + C$ (R = H or Me, n = 1-5)[32b]


(5)

$\log k_\mathrm{R}(\mathrm{acetal}) = 1.7 \log k_\mathrm{R}(\mathrm{vinyl\ ether}) + C$[32c,d]

According to the comparison above the inductivities of the norbornene protonation agree better with the higher inductivities of the solvolyses of *exo*-2-norbornyl tosylates than with the lower inductivities of the endo epimers. The inductivities of the solvolysis of 6-substituted *exo*-2-norbornyl tosylates are abnormally large, but those of the corresponding endo epimers quite normal as compared with those of several other compounds.[1f] Thus the inductivities of protonation of 5-substituted norbornenes are evidently also larger than "normal", although values for a direct comparison are not yet available. According to Grob[1f] there is a clear relationship between the inductivity and the bridging in the transition state of solvolysis: the more significant is the bridging, the larger is the inductivity. Thus the bridging is also probable in the transition state of protonation of norbornenes, and our results support the hypothesis of the nonclassical norbornyl cation. The other hypotheses suggested for the abnormally high reaction rates and/or high exo/endo rate ratios in electrophilic additions to norbornene (see above) do not explain the large inductivities measured. However, they cannot be rejected as contributing factors on the basis of our results.

Summary

Disappearance of 5-X-substituted 2-norbornenes (X = H, CH_2OH, CH_2Cl, Ac, OH, CN, NO_2, and oxo) in aqueous perchloric acid has been divided between the three routes according to their initiation by protonation of X, C-2, and C-3. The proton transfer from a hydronium ion to a substrate is the rate-determining stage in the latter two reactions. In these cases the logarithms of the rate constants obey linearly the inductive substituent constants ($\sigma_\mathrm{I}^\mathrm{q}$) except when the substituents have frangomeric, anchimeric, or initial state-homoconjugation effects. Comparison of the reaction constants (ρ) with those measured by Grob et al. for the solvolyses of 5- and 6-X-substituted *exo*- and *endo*-2-norbornyl tosylates indicates that the ρ values of the norbornene hydration better agree with those of the exo solvolysis than the endo ones. This suggests that the transition state of the norbornene hydration is of a nonclassical character.

I am grateful to the students mentioned in the papers of the author for their active participation in the project as part of their education. Partial financial supports from the Academy of Finland, Research Council for the Natural Sciences, and from the Foundation of the University of Turku are gratefully acknowledged.

---

(32) (a) Allen, A. D.; Ambidge, I. C.; Che, C.; Micheal, H.; Muir, R. J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1983**, *105*, 2343–2350. (b) Data have been collected from several papers. (c) Salomaa, P.; Kankaanperä, A.; Lajunen, M. *Acta Chem. Scand.* **1966**, *20*, 1790–1801. (d) Salomaa, P.; Salmi, J. A., unpublished results on acid-catalyzed hydrolysis of acetals in aqueous acid.

(33) Arnett, E. M.; Petro, C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 522–526.