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Short Communication

Acid-Catalyzed Hydrolysis of Bridged Bi- and Tricyclic Compounds. XXXIV. 3-Methyl-3-nortricyclanol: Kinetics, Products and Mechanism

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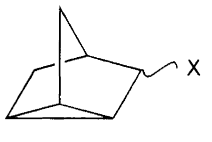
The acid-catalyzed hydration of several 3-*X*-substituted nortricyclanes (**1**) has been studied in our laboratory earlier.[1,2] Usually the reaction is initiated by the rate-determining protonation of the cyclopropane ring ($X =$ H, CH_2OH, CH_2Cl, Ac, OH, OCH_3, CN or NO_2; the Ad_E2 or $A\text{-}S_E2$ mechanism). In a few cases, however, the protonation of the substituent starts the reaction: e.g. when $X = OAc$, the $A_{Ac}2$ ester hydrolysis occurs first; when $X = O$, the cleavage of the cyclopropane ring probably follows an *A*-2 mechanism; and when $X = CH_3OH$, the cleavage of the cyclopropane ring obeys an *A*-1 mechanism. In this last case, attempts were made to solve the real route of the reaction using several methods: reaction rate,[1,3] activation parameters,[3] general acid catalysis,[4] and isotope effects in isotopically different waters,[5] but without result. In the present work, the excess acidity theory[6] and product analysis by modern instruments are used to solve the mechanism of hydrolysis of 3-methyl-3-notricyclanol (**2**) in perchloric acid.



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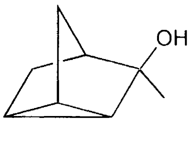

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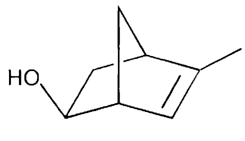

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Syntheses of 3-methyl-3-nortricyclanol[3] (**2**) and 2-methyl-*exo*-5-hydroxy-2-norbornene[7] (**3**) have been reported, the purities by GC being 99.8% and 97%, respectively.

The disappearance of the substrate (**2**) in $HClO_4(aq)$ was followed by GC (an FFAP capillary column) with nitrobenzene as the internal standard and dichloromethane as the extracting solvent.[8] The rate constants of disappearance in aqueous perchloric at 318 K at different acid concentrations are presented in Table 1, and are in good agreement with the rate constants measured earlier in 1 M $HClO_4(aq)$.[1,3]

The rate constants of disappearance increase steeply with increasing acid concentration. This effect can be analyzed quantitatively with the excess acidity theory,[6] which offers eqn. (1)[9]

$$\log k_\psi - \log c_{H^+} = m^{\neq} m^* X_0 - \log[1 + (c_{H^+}/K_{SH^+})10^{m^* X_0}] + \log(k_0/K_{SH^+}) \qquad (1)$$

for the *A*-1 mechanism. In the equation, k_ψ is the pseudo-

Table 1. Rate constants of disappearance for 3-methyl-3-nortricyclanol (**2**) in aqueous perchloric acid at 318.2 K at different acid concentrations.

$c(HClO_4)/M^a$	$X_0{}^b$	$k_\psi/10^{-4}\ s^{-1}$
0.990	0.254	0.966(10)
1.432	0.347	2.065(9)
2.010	0.470	4.79(7)
2.445	0.570	8.62(15)
2.970	0.705	17.34(20)
3.451	0.847	33.0(2)
3.844	0.977	55.8(6)

[a] Temperature corrected. [b] Excess acidity,[10] temperature corrected.[6]

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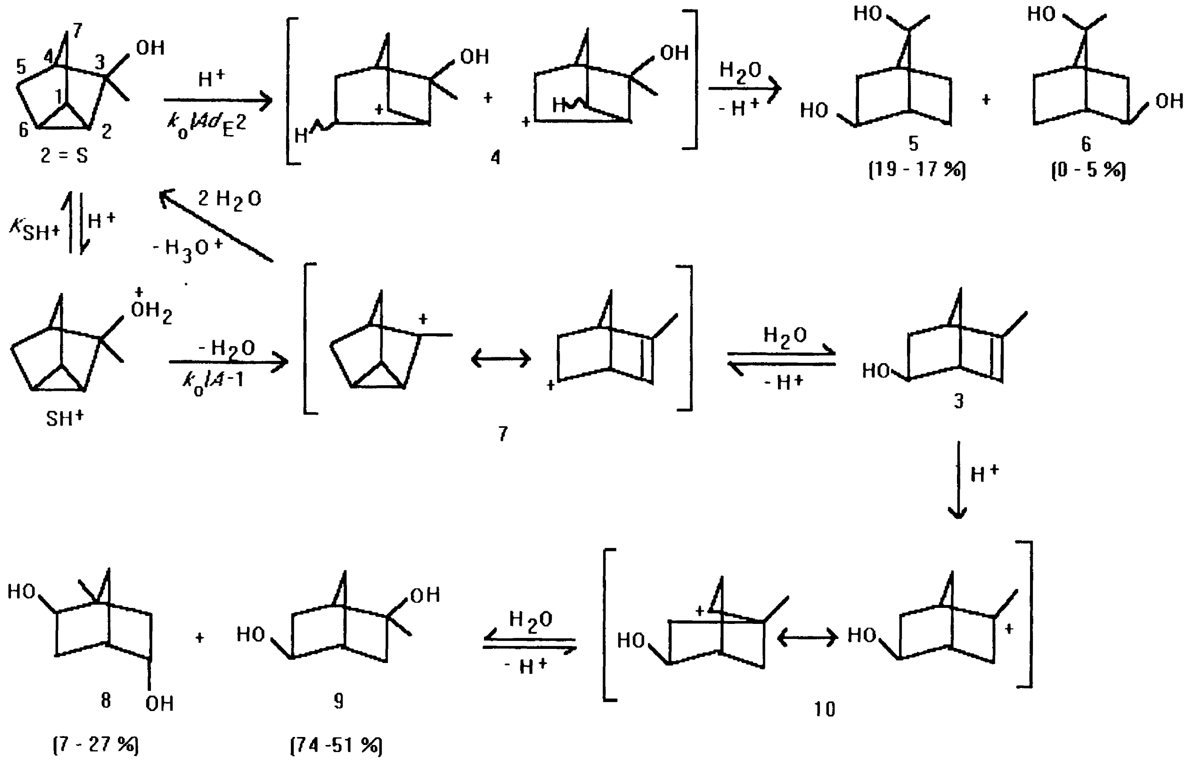

Scheme 1.

first-order rate constant in the aqueous acid of concentration c_{H^+} and of excess acidity X_0;[10] $m^{\neq}$ and m^* are slope parameters, the former being indicative of the transition state and the latter of the site of proton attack; k_0 stands for the medium-independent rate constant of the rate-limiting step of the reaction and K_{SH^+} for the thermodynamic dissociation constant of the oxygen-protonated substrate (Scheme 1).

Equation (1) can be used to evaluate the best values of parameters m^*, $m^{\neq}$, K_{SH^+} (or pK_{SH^+}) and k_0 [or $\log(k_0/K_{SH^+})$] from the experimental values of k_ψ, c_{H^+} and X_0 with the method of nonlinear least-squares minimization. The following values were obtained: $m^* = 1.01 \pm 0.03$, $m^{\neq} = 1.92 \pm 0.05$, $pK_{SH^+} = -1.70 \pm 0.10$ and $\log(k_0/K_{SH^+}) = -4.49 \pm 0.02$, and seem reasonable. The value of m^* is typical of the protonation of the hydroxylic[11] (and ether)[8,9,12] oxygen atom, that of $m^{\neq}$ accords with the A-1 mechanism,[6,9] and the value of pK_{SH^+} is in agreement with those measured earlier for other alcohols[11,13,14] (the tertiary hydroxylic oxygen is evidently more basic than primary or secondary).

Equation (1) can be changed to the original linear form, eqn. (2),[6]

$$\log k_\psi - \log c_{H^+} - \log[c_S/(c_S + c_{SH^+})] = m^{\neq} m^* X_0 + \log(k_0/K_{SH^+}) \qquad (2)$$

for Fig. 1 by the aid of eqn. (3):[6]

$$\log(c_{SH^+}/c_S) - \log c_{H^+} = m^* X_0 + pK_{SH^+} \qquad (3)$$

In the equations, c_S and c_{SH^+} are the concentrations of the substrate, unprotonated and protonated on the oxygen atom. As Fig. 1 shows, the plot is strictly linear ($r = 0.99996$).

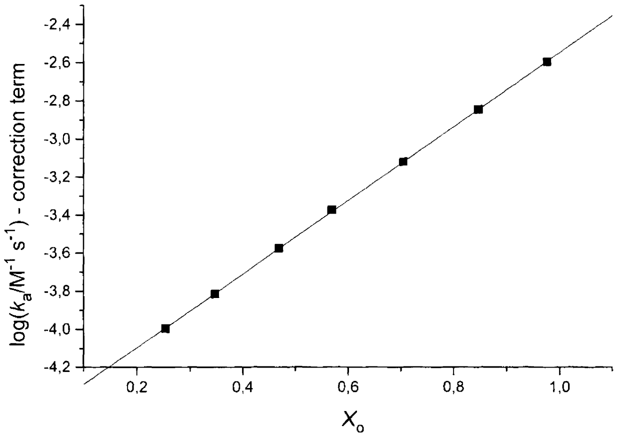

Fig. 1. The excess acidity plot [eqn. (2)] for the hydrolysis of 3-methyl-3-nortricyclanol (**2**) at 318.2 K in $HClO_4$(aq) ($k_a = k_\psi/c_{H^+}$). The correction term, $\log[c_S/(c_S + c_{SH^+})]$, has been calculated with eqn. (3) from the evaluated m^* and pK_{SH^+}.

According to the product analyses,[8] the substrate produces in 1 M $HClO_4$(aq) at ca. 318 K three (ca. 1 $t_{1/2}$) to four (ca. 10 $t_{1/2}$) norbornanediols (Scheme 1), which were identified by GC, GC/FTIR and GC/MS and in the case of the main product, *endo*-2-methyl-*exo,exo*-2,5-norbornanediol (**9**), by ^{13}C NMR ($\delta_{obs} = \delta_{calc}$[15] within 1 ppm). The diol **9** [GC/FTIR: $\nu_{OH} = 3648\ cm^{-1}$ and MS, *m/e* (% rel. int.): e.g. 142 (1, M), 124 (17), 109 (14), 106

(1), 95 (16), 81 (22), 80 (21), 67 (29), 66 (95) and 43 (100)] was also observed to be the predominant hydration product (89%; **5**, **6** and **8** are minor products) of 2-methyl-*exo*-5-hydroxy-2-norbornene (**3**), which reacts ca. 2700 times faster than the substrate **2** in 1 M $HClO_4$(aq) at 298 K.[3,7] It is probable that this unsaturated bicyclic alcohol **3** is a fleeting intermediate in the *A*-1 hydrolysis of **2** (Scheme 1) formed by water attack on the 3-methyl-3-nortricyclyl cation (**7**), which is strongly stabilized by the cyclopropane ring.[16,17] A minor product (**8**; $\nu_{OH} =$ 3663 cm^{-1}), probably 1-methyl-*exo*-2-*endo*-5-norbornanediol, is evidently also formed via the *A*-1 mechanism and the Wagner–Meerwein rearrangement (**10**).[18]

It is probable that the cyclopropane ring of the substrate **2** is also protonated (Ad_E2 mechanism; Scheme 1) in the aqueous acids used, although the portion of this route is of minor importance [$k_{obs} \approx 11 k_{calc}(Ad_E2)$ in 1 M $HClO_4$ at 348 K].[1,3] The protonation mostly takes place on C-1 and C-6 and/or on the σ-bond between these,[1] producing 7-methyl-7-hydroxy-2-norbornyl cations (**4**), which yield the corresponding norbornanediols **5** [$\nu_{OH} =$ 3574 and 3596 cm^{-1} (arising from the intramolecularly hydrogen-bonded and free hydroxyl groups, respectively) and *m/e* 142 (0, M), 124 (38), 109 (16), 106 (2), 95 (20), 81 (100), 80 (74), 67 (20), 66 (9) and 43 (91)] and **6** (3655 cm^{-1}) when reacting with water (Scheme 1). The small yield of these diols (ca. 20% by GC in 1 M $HClO_4$ at 318 K) seems reasonable. Thus the portion of the *A*-1 mechanism is probably 90–80% and that of the Ad_E2 mechanism 10–20% as estimated from the reaction rate and the product analysis, respectively.

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