

Acid-catalyzed Hydrolyses of Bridged Bi- and Tricyclic Compounds. XXI. Kinetics of Hydration of *exo*- and *endo*-5-Nitro-2-norbornenes and 3-Nitronortricyclane

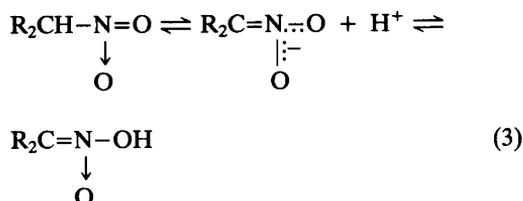
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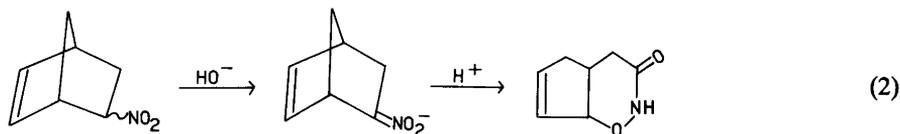
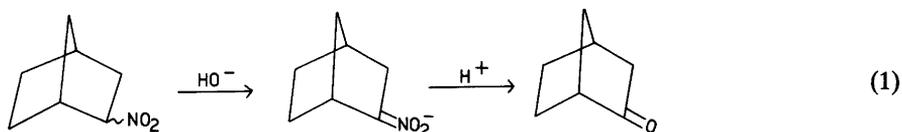
The activation parameters, solvent deuterium isotope effects, and dependences of rates on acid concentration measured for the hydration of *exo*- and *endo*-5-nitro-2-norbornenes and 3-nitronortricyclane agree with the rate-determining protonation of the carbon-carbon double bond or the three-membered carbon ring ($A-S_E2$ mechanism). The product analysis supports the conclusion. The hydration rate of *endo*-5-nitro-2-norbornene seems abnormally high considering the correlation between the hydration rates of 5-X-substituted 2-norbornenes and 3-X-substituted nortricyclanes (X=H, CH₂OH, CH₂Cl, OH, Ac, CN, and NO₂).

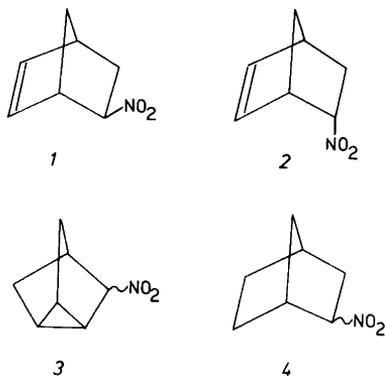
The alkali metal salts of 2-nitronorbornanes and 5-nitro-2-norbornenes react easily with aqueous acids yielding 2-norbornanone (80%) in the former case [the Nef reaction, eqn. (1)] and rearranged products. *e.g.* *cis*-cyclopentena[e]-

tetrahydro-1,2-oxazin-3-one (42%), in the latter case [eqn. (2)].^{1,2} The nitro group is destroyed in both reactions. The reactive structure is evidently the *aci* form of the nitro compound (nitronic acid) formed in the acid-base equilibria [eqn. (3)].³



In the *nitro* form the secondary nitro group is probably much more resistant against aqueous acids. Thus it may be apt for a strongly electronegative substituent in acid-catalyzed hydrolysis reactions. However, the *nitro* form may





produce a minute concentration of the much more energetic *aci* form,³ thus this route must be taken into account.

The present work expands our studies on the acid-catalyzed hydration of substituted norbornenes and nortricyclanes to *exo*- and *endo*-5-nitro-2-norbornenes (1 and 2) and 3-nitronortricyclane (3). The effects of temperature and acid concentration on the reaction rates, and solvent deuterium isotope effects are recorded. The reaction products are also studied and the low reactivity of 2-nitronorbornanes (4) is checked.

EXPERIMENTAL

Syntheses. A mixture of *exo*- and *endo*-5-nitro-2-norbornenes was prepared from cyclopentadiene and nitroethene.² An effort to separate the epimers on a preparative gas chromatograph (FFAP column) caused the isomerization of the 1:4 mixture producing a new one where the *exo* and *endo* epimers had the equilibrium ratio of ca. 2:1 (cf. Ref. 4). The *exo* epimer was obtained from this mixture with the purity of 95 % by GLC. The *endo* epimer used in the investigations contained ca. 17 % of the *exo* form. The retention times (*exo* 5.6 min and *endo* 8.1 min in a FFAP column at 130 °C) were so different that the epimers did not disturb each other.

3-Nitronortricyclane was prepared as follows. The addition of acetic acid to 2,5-norbornadiene produced a mixture of *exo*-5-acetoxy-2-norbornene and 3-acetoxynortricyclane.⁵ The acetates were separated by distillation on a Perkin Elmer 251 Auto Annular Still and the tricyclic acetate was hydrolyzed by aqueous potassium hydroxide to 3-hydroxynortricyclane, which was oxidized to 3-nortricyclanone.⁶ The ketone was turned to the

corresponding oxime by hydroxylamine hydrochloride.⁷ The oxime was recrystallized from liquid petroleum (b.p. 50–70 °C) and oxidized to 3-nitronortricyclane by the method of Emmons and Pagano,⁸ but the oxidant used by them, peroxytrifluoroacetic acid, was replaced by 3-chloroperbenzoic acid. The yield was 63 % from the oxime, which is of the same magnitude as those obtained by peroxytrifluoroacetic acid oxidation of aliphatic oximes,⁸ and 24 % from the starting materials.

A mixture (*exo*–*endo*=1:5) of 2-nitronorbornanes was prepared by hydrogenating the corresponding mixture of 5-nitro-2-norbornenes in acetone with palladium on carbon as catalyst at room temperature and in atmospheric pressure.

The substrates were identified from their IR (NO₂: 1545 and 1375 cm⁻¹) and ¹H and/or ¹³C NMR spectra.^{4,9,10}

Kinetics. The disappearance of the substrates (initial concentration 3×10⁻³ mol dm⁻³) in aqueous perchloric acid was followed during about 2.5 half-lives by taking samples after appropriate intervals, by neutralizing them with concentrated ammonia and Sørensen phosphate buffer (pH 6.8), and by analyzing them by GLC (FFAP column) using camphor as inert internal standard. The *exo* and *endo* epimers isomerized quite easily to each other in the gas chromatograph. The very careful manner of working reduced but did not totally eliminate the epimerization, which caused scattering in rate constants. Thus the standard errors of the mean were larger for nitronorbornenes (2–4 %, av. 3 %) than for nitronortricyclane (1–2 %, av. 1.3 %). Several duplicate or triplicate runs, however, showed that the measured rate coefficients were reproducible within 10 %. The reaction medium turned slightly reddish brown during the runs and in the case of nitronorbornenes small dark brown flakes appeared during long runs (*t*_{1/2}≥5 h).

Product analysis. 0.70 g of a 1:5 mixture of *exo*- and *endo*-5-nitro-2-norbornenes was hydrolyzed over ten half-lives by efficiently stirring in 50 cm³ of 5 mol dm⁻³ HClO₄ at 75 °C. The solution was cooled and extracted with CH₂Cl₂ four times. The organic phase was washed with water three times and dried on sodium sulphate. The solvent was distilled off *in vacuo* and the residue (0.40 g) was analyzed by GLC and by IR, ¹H and ¹³C NMR spectroscopy: the product was a 48:52 (±2) mixture of *exo*- and *endo*-5-nitro-*exo*-2-norbornenes (see Table 1).

The solid flakes were separated from the aqueous phase after extraction with CH₂Cl₂ by repeatedly decanting acidic water off and by adding fresh water until the solvent was neutral,

Table 1. Comparison of the ^{13}C chemical shifts for *exo*- and *endo*-5-nitro-*exo*-2-norborneols (calculated by addition of the effects of the *exo*-2-hydroxyl and *exo*- and *endo*-5-nitro groups on the chemical shifts of norbornane) with the observed ^{13}C chemical shifts in CDCl_3 for the product of hydration of *exo*- and *endo*-5-nitro-2-norbornenes.

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	Ref.
Norbornane	36.8	30.1	30.1	36.8	30.1	30.1	38.7	10
$\Delta\delta(\textit{exo}$ -2-OH)	+7.7	+44.3	+12.3	-1.0	-1.3	-5.2	-4.1	10
$\Delta\delta(\textit{exo}$ -5- NO_2)	+0.2	-2.0	-3.7	+6.8	+58.0	+5.7	-2.9	^a
$\Delta\delta(\textit{endo}$ -5- NO_2)	± 0.0	-1.8	-7.0	+6.1	+57.5	+3.3	+0.2	^a
<i>exo</i> -5-Nitro- <i>exo</i> -2-norborneol (calc.)	44.7	72.4	38.7	42.6	86.8	30.6	31.7	
<i>exo</i> -5-Nitro- <i>exo</i> -2-norborneol (obs.)	43.6	72.7	38.3	42.7	86.9	31.7	31.7	^a
<i>endo</i> -5-Nitro- <i>exo</i> -2-norborneol (calc.)	44.5	72.6	35.4	41.9	86.3	28.2	34.8	
<i>endo</i> -5-Nitro- <i>exo</i> -2-norborneol (obs.)	44.3	72.8	35.5	42.0	85.8	29.1	34.9	^a

^a This work.

thereafter the flakes were filtered off and dried (yield 20 mg). According to the IR spectrum the nitro group had mainly but not entirely disappeared and a hydroxyl group had appeared.

RESULTS AND DISCUSSION

The disappearance rate coefficients of *exo*- and *endo*-5-nitro-2-norbornenes (1 and 2) and 3-nitronorbornene (3) in 5 mol dm^{-3} perchloric acid at different temperatures are listed in Table 2 together with the activation parameters calculated from the second-order rate coefficients ($k_2 = k_1/c_{\text{HClO}_4}$). The solvent deuterium isotope effects are also given. The activation entropies (-18 to -39 J mol^{-1} K^{-1}) and isotope effects ($k_{\text{H}}/k_{\text{D}}$ 1.1 to 1.2) are in agreement with the rate-determining proton transfer from the hydronium ion to the carbon-carbon double bond of the nitronorbornenes and to the three-membered carbon ring of nitronorbornene ($A-S_{\text{E}2}$ or $A_{\text{D}}\text{E}2$ mechanism), but not with the initial protonation of the nitro group ($A-1$ or $A-2$ mechanisms).¹¹⁻¹⁵ The isotope effects are close to unity, which points to a late "intermediate-like" transition state. This agrees, according to the Hammond postulate,¹⁶ with the slow reaction rate caused by the very electronegative nitro group. In the $A-S_{\text{E}2}$ hydration of *exo*- and *endo*-5-cyano-2-norbornenes and 3-cyanonorbornene, where the reaction rates are equal or slightly greater ($k_1/10^{-4}$ s $^{-1}$: 11.4, 10.25 and 20.0, respectively, in 5 mol dm^{-3} HClO_4 at 75 °C), the isotope effects are, however, larger: 1.4 to 1.6.¹²

The disappearance rate constants in different

Table 2. Rate constants for the disappearance of 5-nitro-2-norbornenes, 3-nitronorbornene, and 2-nitronorbornanes in aqueous 5.03 mol dm^{-3} HClO_4 at different temperatures, and their solvent deuterium isotope effects at 75 °C and activation parameters at 25 °C.

Temp. °C	k_1 10^{-4} s $^{-1}$	Isotope effects and activation parameters
<i>exo</i> -5-Nitro-2-norbornene		
25	0.0169 ^a	
45	0.234	
55	0.698	$k_{\text{H}}/k_{\text{D}}=1.09(7)$
65	2.08	$\Delta H^\ddagger=99.8(26)$ kJ mol^{-1}
75	6.49	$\Delta S^\ddagger=-34(8)$ J mol^{-1} K^{-1}
75	5.93 ^b	
<i>endo</i> -5-Nitro-2-norbornene		
25	0.0261 ^a	
45	0.385	
55	1.240	$k_{\text{H}}/k_{\text{D}}=1.11(5)$
65	4.10	$\Delta H^\ddagger=103.5(12)$ kJ mol^{-1}
75	11.68	$\Delta S^\ddagger=-18(4)$ J mol^{-1} K^{-1}
75	10.47 ^b	
3-Nitronorbornene		
25	0.00884 ^a	
55	0.383	
65	1.116	$k_{\text{H}}/k_{\text{D}}=1.22(4)$
75	3.32	$\Delta H^\ddagger=99.9(11)$ kJ mol^{-1}
75	2.73 ^b	$\Delta S^\ddagger=-39(3)$ J mol^{-1} K^{-1}
85	8.58	
2-Nitronorbornanes (<i>exo</i> - <i>endo</i> =1:5)		
75	0.0175(6)	

^a Calculated from the activation parameters. ^b Measured in 5.01 mol dm^{-3} $\text{DClO}_4(\text{D}_2\text{O})$.

Table 3. Rate constants for the disappearance of *exo*- and *endo*-5-nitro-2-norbornenes at 75 °C and 3-nitronorbornene at 85 °C in different perchloric acid concentrations, and slopes for the plots $\log k_1$ vs. $-H_o$ (Slope) and $\log k_1 + H_o$ vs. $H_o + \log c_{\text{HClO}_4}$ (ϕ).

$\frac{c_{\text{HClO}_4}}{\text{mol dm}^{-3}}$	$-H_o$	$\frac{k_1}{10^{-4} \text{ s}^{-1}}$	Slopes
<i>exo</i> -5-Nitro-2-norbornene			
0.996	0.33	0.0463	Slope=1.09(1) $\phi=-0.13(2)$
2.05	0.84	0.166	
3.03	1.33	0.600	
4.02	1.81	1.85	
5.03	2.33	6.49	
6.02	2.92	33.0	
<i>endo</i> -5-Nitro-2-norbornene			
1.002	0.33	0.203	Slope=0.98(1) ^a $\phi=0.02(1)$ ^a
2.02	0.83	0.403	
3.03	1.33	1.28	
4.02	1.81	3.76	
5.03	2.33	11.68	
6.02	2.92	46.4	
3-Nitronorbornene			
1.002	0.33	0.0529	Slope=1.04(2) $\phi=-0.05(3)$
2.02	0.83	0.208	
3.03	1.33	0.697	
4.02	1.81	2.36	
5.03	2.33	8.58	
6.02	2.92	30.8	
7.04	3.55	120.5	

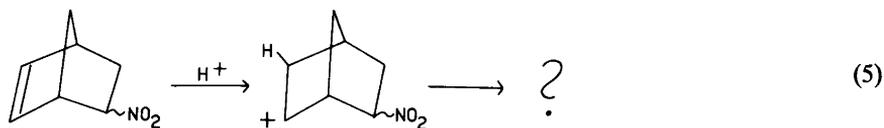
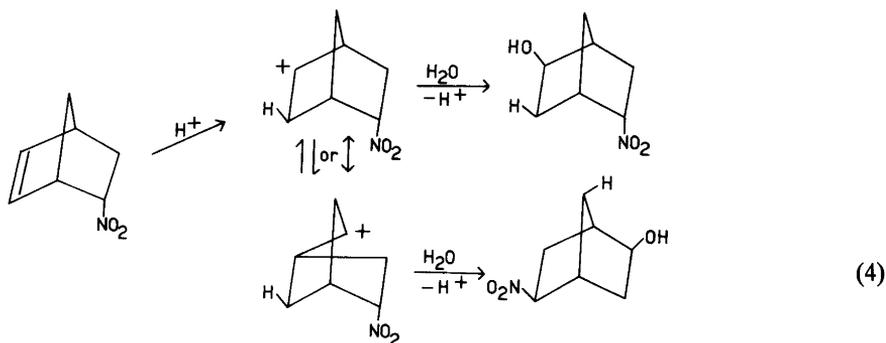
^a An exceptional value in 1.00 mol dm⁻³ HClO₄ has been excluded.

acid concentrations are listed in Table 3 together with the slopes for the plots $\log k_1$ vs. $-H_o$ and $\log k_1 + H_o$ vs. $H_o + \log c_{\text{HClO}_4}$. The former plots are fairly linear (correlation coefficients 0.9992 to 0.9999) and their slopes (0.98 to 1.09) are typical of the *A-S_E2* mechanism as are also the Bunnett-Olsen ϕ values (the slopes of the latter plots: -0.13 to $+0.02$).^{11-15,17}

All the kinetic parameters are thus in agreement with the hydration of the carbon-carbon double bond and the three-membered carbon ring of the substrates. The rate constants are 190–670 times greater than the disappearance rate constant of 2-nitronorbornane (an *exo-endo* mixture; see Table 2). 2-Nitronorbornane yields 2-norbornanone [analyzed by GLC; cf. eqns. (1) and (3)]. Thus this rate constant gives a rough estimate of the reaction *via* the *aci* form, and it seems negligible.

The product analysis for the hydrolysis of nitronorbornenes (*exo-endo*=1:5) showed that the reaction yields at least 50 % of 5-nitro-*exo*-2-norborneols (*exo-endo*=1:1; see Experimental) probably *via* protonation of C(3), Wagner-Meerwein rearrangement, and hydration of C(2) [eqn. (4)].

Besides, ca. 3 % of an unidentified saturated polymeric product was isolated. Other products were not observed, but the formation of up to 50 % of rearranged and/or fragmented products (soluble in acidic water but insoluble in CH₂Cl₂ and invisible in the GLC analysis of the neutralized samples), e.g. *via* protonation of C(2) [eqn. (5)], can not be entirely excluded (cf. Ref. 18).



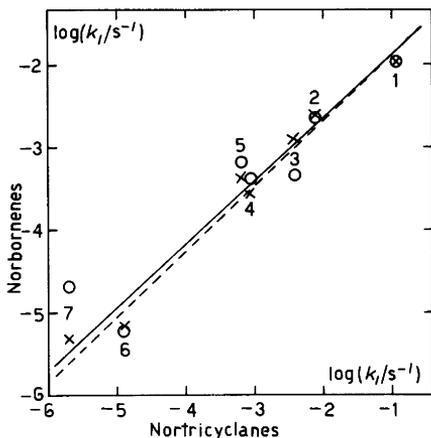


Fig. 1. The logarithms of rate constants of hydration for *exo*- and *endo*-5-substituted 2-norbornenes versus those for 3-substituted nortricyclanes (1 mol dm⁻³ HClO₄ at 75 °C). Symbols: ×, *exo* substituent and ○, *endo* substituent; 1, hydrogen; 2, hydroxymethyl; 3, chloromethyl (unpublished preliminary values); 4, hydroxyl; 5, acetyl (unpublished values); 6, cyano, and 7, nitro; —, *exo*-substituted norbornenes (slope=0.765, *r*=0.989) and ---, *endo*-substituted norbornenes (slope=0.794, *r*=0.965, point No. 7 has been excluded).

There is a hint of a possible side reaction in the case of *endo*-5-nitro-2-norbornene (2). It is a somewhat exceptional behavior of *endo*-nitronorbornene in the otherwise fairly linear correlation between the logarithms of rate constants for 5-substituted 2-norbornenes and 3-substituted nortricyclanes in 1 mol dm⁻³ HClO₄ at 75 °C (Fig. 1). The observed disappearance rate of *endo*-nitronorbornene (Table 3) is about eight times greater than the predicted value. However, this high rate is in the agreement with the observation made by Grob *et al.* that the solvolysis rate of *endo*-6-nitro-*exo*-2-norbornyl tosylate is abnormally high (42 times greater than that of *exo*-6-nitro-*exo*-2-norbornyl tosylate).¹⁸ The reason may be the same, *e.g.* the neighboring-group participation of the oxygen atoms of the *endo* nitro group.

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