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Acid-catalyzed Hydrolyses of Bridged Bi- and Tricyclic Compounds. I. Kinetics and Product Analyses of Some 2-Norbornyl, 2-Norbornenyl, and 3-Nortricyclyl Acetates*

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The hydrolysis of *exo* and *endo* isomers of several secondary and methyl-substituted tertiary 2-norbornyl and 2-norbornenyl acetates and of secondary and tertiary 3-nortricyclyl, cyclopentyl, and cyclohexyl acetates has been studied by titrimetric and gas-chromatographic methods under catalysis by perchloric acid (1 M in 60 wt. % dioxane – water). All secondary acetates were observed to hydrolyze by the $A_{AC}2$ mechanism and the tertiary acetates by the $A_{AL}1$ mechanism with the exception of the tertiary *endo*-2-norbornenyl acetate, which hydrolyzes simultaneously by both mechanisms. Solvent deuterium isotope effects measured for some acetates agree with these mechanisms. "Normal" rates of hydrolysis *via* carbenium ions were estimated for the tertiary acetates by a modified Schleyer method. A notable anchimeric increase in the rate of hydrolysis was evaluated for the *exo* and tricyclic acetates, but the rate of hydrolysis was estimated to be "normal" in the case of the *endo* acetates.

2-Norbornyl and 2-norbornenyl esters, especially sulfonates, have been the subject of intensive solvolysis studies during recent decades.[2–10] Characteristic of these solvolysis reactions, which usually follow the S_N1 mechanism, are (a) high *exo*/*endo* rate ratios, (b) rearranged *exo* and/or tricyclic products, and (c) the formation of solely (*exo* substrates) or nearly solely (*endo* substrates) racemic products in the reaction of optically active precursors. These characteristics have been explained to be due to the formation of nonclassical carbonium ions (delocalized positive charge) from *exo* substrates and the formation of classical carbenium ions (localized positive charge) from *endo* substrates.[2–6] These deductions have, however, encountered strong criticism.[6–11]

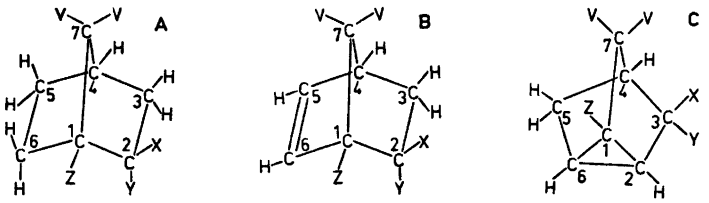
The acid-catalyzed hydrolyses of the simple carboxylic acid esters of 2-norborneols and 2-norbornenols have been studied much more seldom.[12–14] It is possible that *exo* carboxylates favor the $A_{AL}1$ hydrolysis,[15] in which the stable carbonium ion of nonclassical character may be formed from the protonated substrate in the rate-determining step of the reaction, whereas *endo* carboxylates may, in order to avoid the sterically hindered transition state of the $A_{AL}1$ hydrolysis,[7–10] hydrolyze by the $A_{AC}2$ mechanism,[15] in which one or more molecules of water react with the protonated substrate in the rate-determining step. For this study several 2-norbornyl, 2-norbornenyl, and 3-nortricyclyl acetates (Table 1) and cyclopentyl (Pent-I-OAc), 1-methylcyclopentyl (Pent-II-OAc), cyclohexyl (Hex-I-OAc), and 1-methylcyclohexyl (Hex-II-OAc) acetates were prepared. The hydrolysis rates of the acetates were measured at several temperatures in a solution of 1.00 M perchloric acid in 60 wt. % dioxane-water. The products of hydrolysis were analyzed.

EXPERIMENTAL

The preparation and identification of the bi- and tricyclic acetates and the corresponding alcohols is described in Ref. 1. The reaction medium, consisting of water and dioxane in the

* Part 1 of the abridgment of M. Lajunen's Dissertation.[1]

Table 1. The numbering system and symbols used in this paper for 2-norbornyl (A), 2-norbornenyl [a] (B), and 3-nortricyclyl (C) acetates and alcohols.



V	X	Y	Z	A	B	C
H	x[b]	H	H	*exo*-I-x	*exo*-V-x	X-x[c]
H	H	x	H	*endo*-I-x	*endo*-V-x	X-x[c]
H	x	R[d]	H	*exo*-II-x	*exo*-VI-x	XI-x[e]
H	R	x	H	*endo*-II-x	*endo*-VI-x	XI-x[e]
H	x	H	R	*exo*-III-x		*cis*-XII-x
H	H	x	R	*endo*-III-x		*trans*-XII-x
R	x	H	R	*exo*-IV-x		
R	H	x	R	*endo*-IV-x		

[a] The site of the double bond between C(5) and C(6) is not indicated with a number in this paper. [b] x indicates OH or OAc. [c] Enantiomers. [d] R indicates the methyl group. [e] Enantiomers.

weight ratio 40:60, was prepared by weighing the components.

Kinetic measurements were performed partly titrimetrically by following the formation of acetic acid and partly by gas chromatography (columns: 5 % FFAP on Chromosorb G, 10 % XE-60 on Chromosorb W, and 10 % Versamid 900 on Chromosorb W) when the disappearance of the acetates and the formation and possible decomposition of the alcohols were followed. In the hydrolyses of tricyclic and unsaturated bicyclic acetates the alcohols produced are unstable and react further with the medium when norbornanediols are formed (*cf.* Ref. 16). In these consecutive reactions $A \xrightarrow{k_A} B \xrightarrow{k_B} C$ the rate of decomposition of A into B (k_A) was determined by iteration using variations of eqn. (1) derived for the concentration of

$$[B] = \frac{k_A[A]_0}{k_B - k_A}[\exp(-k_A t) - \exp(-k_B t)] + [B]_0 \exp(-k_B t) \quad (1)$$

B at time t.[17] (Initial conditions are $[A] = [A]_0$ and $[B] = [B]_0$ at $t = 0$.) The disappearance rate of B (k_B) was determined separately. The intermediate products were analyzed by gas chromatography (GLC) and IR and NMR spectroscopy.[1] Norbornanediols were not identified. The observed disappearance rates of the acetates and the unsaturated and tricyclic alcohols studied are given in Tables 2 – 3. The intermediate and final products, which could be detected by GLC during ten half-lives of the reaction, are also given.

The side reactions, in which water adds by acid catalysis to the double bond of 2-norbornenyl acetates (*cf.* k_D in Scheme 1) and to the three-membered carbon ring of 3-nortricyclyl acetates, were estimated to be insignificant (rate coefficients in Tables 2 – 3 and the inductive constants of acetoxyl and hydroxyl groups [18] have been compared).[1] The same results were achieved experimentally when the kinetic response ratios (RR_{kin}, eqn. 2) were compared with the response ratios of acetates and the corresponding alcohols in their equimolar solutions (RR, eqn. 3).

$$RR_{kin} = \frac{a^0_{AC} + \sum RR_i a^0_{AI,i}}{\sum a^\infty_{AI,i} + a^\infty_{AC}/RR} \quad (2)$$

$$RR = \frac{a_{AC}(\text{n mol/l})}{a_{AI}(\text{n mol/l})} \quad (3)$$

In the equations a_{AC} and a_{AI} are the GLC peak areas of acetate and alcohol(s), respectively, and the superscripts 0 and ∞ refer to the first ($t = 0$) and the final ($t = 10t_{1/2}$) samples (a^∞_{AC} was 0 – 2 % of the value of a^0_{AC}). RR_{kin} was observed to be equal to RR ($= 1.24 \pm 0.01$) within experimental error (with the exception of *endo*-VI-OAc) when the peak areas of tricyclic alcohols formed in the hydrolysis of bicyclic acetates were corrected to correspond

Table 2. Rates and products of acid-catalyzed hydrolyses of some mono-, bi-, and tricyclic acetates in a solution of 1.00 M perchloric acid in 60 wt. % dioxane-water at different temperatures.

Acetate	$10^5 k_a/M^{-1}s^{-1}$ [a] 15 °C	25 °C	35 °C	45 °C	55 °C	Products
Pent-I-OAc		4.58	11.2	26.0	56.8	Pent-I-OH
Hex-I-OAc		4.83	11.2	26.2	57.6	Hex-I-OH
exo-I-OAc		3.90	9.06	22.0;28.1 [b]	50.4	*exo*-I-OH
endo-I-OAc		4.70	11.3	25.9	54.4	*endo*-I-OH
exo-III-OAc		2.95	6.38	14.9	33.3	*exo*-III-OH and II-OH
endo-III-OAc		3.38	7.78	18.3	39.9	*endo*-III-OH
exo-IV-OAc [c]		0.35 [d]				
endo-IV-OAc [c]		3.08				
iso-Pr-OAc [c]		4.7				
exo-V-OAc		3.72	9.11	21.4	47.8	*exo*-V-OH and some X-OH [e] and unknown subst.
endo-V-OAc		3.90	9.76	22.5	48.5	*endo*-V-OH and some [e] unknown substance
X-OAc		7.50	17.3	38.1	85.7	X-OH [e]
Pent-II-OAc	8.65	37.9	157	547		Pent-II-OH and 12–15 % of 1-methylcyclopentene
Hex-II-OAc		3.65	16.5	73.5	290	Hex-II-OH and 28–36 % of 1-methylcyclohexene
tert-BuOAc [c]		3.44				
exo-II-OAc	26.5 [f]	85.9 [b,f]	148 [g]	637 [h]		*exo*-II-OH and some *endo*-II-OH and *exo*-III-OH
	66.0	327	1130			
exo-II-OAc [i]	6.80 [f]	50.6	216	780		
	26.6 [g]					
endo-II-OAc		0.477	1.65	6.21	17.8	*exo*- and *endo*-II-OH and *exo*-III-OH
					50.9 [b]	
exo-VI-OAc	3.97	17.2	77.8	321		*exo*-VI-OH and XII-OH [e]
endo-VI-OAc		0.622	1.68	4.16	11.4	*endo*-VI-OH and XII-OH [e] (perhaps some *exo*-VI-OH)
XI-OAc	7.82 [f]	34.2 [g]	149 [h]	568 [j]		XI-OH [e]
	18.3	69.6	276	1060		

[a] The standard errors are 1–3 % of the value of the rate coefficients. [b] A solution of 1.00 M deuterioperchloric acid in 57.4 wt.% dioxane-heavy water. The mol fraction of deuterium oxide is the same as that of protium oxide in a solution of 1.00 M protioperchloric acid in 60 wt.% dioxane-light water. [c] Results of Bunton *et.al.*[12] in 60 % by volume dioxane-water. [d] Extrapolated. [e] The final products are norbornanediols. [f] 10°C. [g] 20°C. [h] 30°C. [i] Measured in 0.258–0.260 M acid concentrations. [j] 40°C.

Table 3. Rates and intermediate products of acid-catalyzed decomposition of unsaturated bicyclic and tricyclic alcohols in a solution of 1.00 M perchloric acid in 60 wt. % dioxane-water at 45 and 55 °C.

Alcohol	Temp./°C	$10^5 k_a/M^{-1}\,s^{-1}$	Intermediate products [a]
exo-V-OH	55	0.314 ± 0.008	*ca.* 20 % of X-OH and *ca.* 6 % of unknown substance
endo-V-OH	55	0.789 ± 0.012	*ca.* 4 % of unknown substance
X-OH	55	1.24 ± 0.02	
exo-VI-OH	55	73.7 ± 1.7	90–100 % of XII-OH [b]
endo-VI-OH	55	1.74 ± 0.02	29 % of XII-OH [c]
	45	0.403 ± 0.005	23 % of XII-OH [c]
XI-OH	55	7.19 ± 0.09	
XII-OH (*cis:*	55	5.19 ± 0.07	Some unknown
trans = 1:2)	45	1.49 ± 0.01	substance

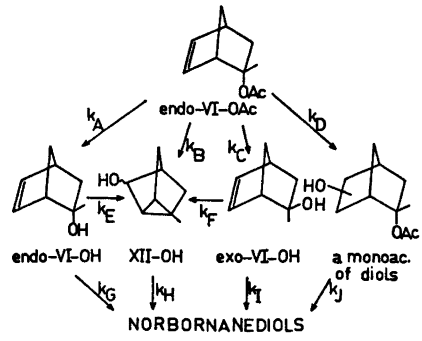
[a] The final products are norbornanediols. [b] Percentage of XII-OH $= 100k_F/(k_F + k_I)$, see Scheme 1. [c] Percentage of XII-OH $= 100k_E/(k_E + k_G)$, see Scheme 1.

to those of bicyclic alcohols by multiplying the former areas with the factor $a_{bic-OH}/a_{tric-OH}$ (= 1.10) determined in the equimolar alcohol mixture (norbornanediols were not included when calculating RR_{kin} values). The observed RR_{kin} values also indicate that the decomposition (isomerization excluded) of the product alcohols is slight during the first ten half-lives of the hydrolysis reactions of the acetates with the exception of *endo*-VI-OAc.

DISCUSSION

The products of acid-catalyzed hydrolysis of secondary mono-, bi-, and tricyclic acetates were generally observed to be the corresponding alcohols (Table 2). The isomeric alcohols formed as by-products in the hydrolyses of 1-methyl-*exo*-2-norbornyl (*exo*-III-OAc) and *exo*-2-norbornenyl (*exo*-V-OAc) acetates could be proved to be the isomerization products of initially formed *exo*-III-OH and *exo*-V-OH (Table 3), respectively. With the exception of 3-methyl-3-nortricyclyl acetate (XI-OAc) all the tertiary acetates produce in addition to the corresponding alcohols other products (excluding norbornanediols; Table 2). 2-Methyl-2-norbornyl acetates (*exo*- and *endo*-II-OAc) produce in addition to 2-methyl-2-norborneols (II-OH; *exo* and *endo* isomers could not be separated by GLC) 1-methyl-*exo*-2-norborneol (*exo*-III-OH), the proportion of which in the products increases during the reaction (thermodynamic control; *cf.* Refs. 19 and 20). *Exo*-II-OH was verified by IR spectroscopy to be the only initially formed product of *exo*-II-OAc, but it could not be proved to be the only product of kinetic control in the hydrolysis of *endo*-II-OAc due to the complexity of the IR spectra of the mixture of the substrate and products. However, it is the main product, which isomerizes into *endo*-II-OH and *exo*-III-OH during the course of the slow hydrolysis.

In the hydrolyses of 2-methyl-2-norbornenyl acetates (*exo*- and *endo*-VI-OAc) 1-methyl-3-nortricyclanols (XII-OH; *cis* and *trans* isomers could not be separated by GLC) were formed in addition to the bicyclic alcohols (*exo*- and *endo*-VI-OH, respectively). The proportion of XII-OH in the products increases during the reaction. Thus they are at least partly the product of thermodynamic control. In the hydrolysis of *exo*-VI-OH it is not possible, owing to the few experiments, to draw any conclusion about how much of the tricyclic products is formed directly from the *exo* acetate and how much as the isomerization product of *exo*-VI-OH. *Exo*-VI-OH produces XII-OH much faster than it produces norbornanediols. The subject needs more study. The hydrolysis products of *endo*-VI-OAc could be analyzed more accurately (Scheme 1). By using an iterative procedure,



Scheme 1.

based on eqn. (1), and the disappearance rates in Tables 2 – 3 the rate constants in Table 4 could be evaluated. According to the results both *endo*-VI-OH and XII-OH (and possibly some *exo*-VI-OH) are formed under kinetic control, but XII-OH (and possibly *exo*-VI-OH) is also partly the isomerization product of *endo*-VI-OH. The reverse reactions

exo-VI-OH → *endo*-VI-OH ← XII-OH

could not be observed.

The formation of olefins, which was observed in the hydrolysis of 1-methylcyclopentyl (Pent-II-OAc) and 1-methylcyclohexyl (Hex-II-OAc) acetates, was not detected by GLC in the hydrolysis of the bi- and tricyclic acetates (*cf.* Ref. 21).

The Arrhenius equation was observed to be valid for all the acetates within the limits of the rather narrow temperature range employed in this study. The activation parameters and the calculated rate coefficients at 25 °C are presented in Table 5. The secondary mono-, bi-, and tricyclic acetates greatly resemble each other in their rates of hydrolysis and parameters of activation. They are typical of the $A_{AC}2$ hydrolysis.[15] The solvent deuterium isotope

Table 4. The values for the rate constants in Scheme 1 in a solution of 1.00 M perchloric acid in 60 wt. % dioxane-water at 45 and 55 °C.

Temp./°C	$10^5 k_a/M^{-1}\,s^{-1}$							
	k_A	k_B+k_C	k_D[a]	k_E	k_F	k_G	k_H	k_I
45	2.41	1.75	$\lesssim 0.05$	0.095	–	0.308	1.49	–
55	5.68 6.03	5.5	$\lesssim 0.2$	0.497	*ca.* 73	1.24	5.19	*ca.* 1

[a] Estimated from k_G on the basis of inductive effects of the substituents at the 2 position.[1]

Table 5. Thermodynamic functions of activation and calculated rate coefficients for the hydrolyses of mono-, bi-, and tricyclic acetates in a solution of 1.00 M perchloric acid in 60 wt. % dioxane-water at 25 °C.

Acetate	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	$10^5 k_a/M^{-1}s^{-1}$
Pent-I-OAc	15.7 ± 0.1	−25.6 ± 0.1	4.58 ± 0.01
Hex-I-OAc	15.5 ± 0.2	−26.3 ± 0.6	4.75 ± 0.09
exo-I-OAc	16.1 ± 0.3	−24.9 ± 1.0	3.79 ± 0.12
endo-I-OAc	15.3 ± 0.1	−27.0 ± 0.4	4.72 ± 0.05
exo-III-OAc	15.2 ± 0.5	−28.4 ± 1.5	2.84 ± 0.13
endo-III-OAc	15.5 ± 0.2	−27.2 ± 0.7	3.32 ± 0.07
exo-IV-OAc[a]	17.5[b]	−28[b]	0.35
endo-IV-OAc[a]	15[b]	−31[b]	3.08
iso-Pr-OAc[a]	16.5	−25	4.5
exo-V-OAc	16.0 ± 0.1	−25.3 ± 0.2	3.70 ± 0.02
endo-V-OAc	15.7 ± 0.1	−25.9 ± 0.4	3.94 ± 0.05
X-OAc	15.2 ± 0.2	−26.6 ± 0.8	7.38 ± 0.17
Pent-II-OAc	24.8 ± 0.2	+ 8.8 ± 0.8	37.9 ± 0.6
Hex-II-OAc	27.8 ± 0.2	+14.5 ± 0.7	3.58 ± 0.07
tert-BuOAc[a]	25.5	− 1	3.44
exo-II-OAc	25.6 ± 0.7	+15.6 ± 2.4	299 ± 11
»	23.8 ± 0.6[c]	+ 6.5 ± 1.9[c]	55.7 ± 2.1[c]
endo-II-OAc	23.1 ± 0.5	− 5.4 ± 1.6	0.472 ± 0.024
exo-VI-OAc	26.2 ± 0.5	+12.1 ± 1.5	18.2 ± 0.6
endo-VI-OAc (tot)	18.3 ± 0.3	−21.1 ± 1.0	0.601 ± 0.020
» ($A_{AL}1$)	23.2 ± 1.1	− 8 ± 3	0.14 ± 0.02
» ($A_{AC}2$)	17.8 ± 1.1	−24 ± 3	0.34 ± 0.05
XI-OAc	24.4 ± 0.3	+ 8.9 ± 0.9	73.2 ± 1.3

[a] Results of Bunton *et.al.*[12] in 60 % by volume dioxane-water. [b] Measured in 0.1 − 0.3 M acid concentrations. [c] Measured in 0.258 − 0.260 M acid concentrations.

effect measured for *exo*-2-norbornyl acetate (*exo*-I-OAc), 1.28 at 45 °C, also agrees with this mechanism.[22] The rates of hydrolysis and the activation parameters measured for the tertiary mono-, bi-, and tricyclic acetates differ remarkably from each other. With the exception of the values for *exo*-2-methyl-*endo*-2-norbornenyl acetate (*endo*-VI-OAc) they are typical of the $A_{AL}1$ hydrolysis.[15] The solvent deuterium isotope effects measured for the 2-methyl-2-norbornyl acetates (*exo*-II-OAc: 3.24 at 10 °C and *endo*-II-OAc: 2.86 at 55 °C) are also consistent with this mechanism.[22] The observed activation parameters of *endo*-VI-OAc are close to the typical values of the $A_{AC}2$ mechanism, but they are, however, somewhat higher than those of the secondary acetates in Table 5. The above observations of hydrolysis products agree with the simultaneous contribution of two mechanisms, *viz.* $A_{AL}1$ and $A_{AC}2$: both *exo*-2-

methyl-*endo*-2-norbornenol (*endo*-VI-OH) and 1-methyl-3-nortricyclanols (XII-OH) as well as possibly some *endo*-2-methyl-*exo*-2-norbornenol (*exo*-VI-OH) are formed as the products of kinetic control. No observations have been made that simple *endo*-2-norbornyl and *endo*-2-norbornenyl esters produce *endo* products in the solvolysis *via* carbonium ions.[2-10] So *endo*-VI-OH can be explained to be formed in the $A_{AC}2$ hydrolysis and XII-OH (and *exo*-VI-OH) in the $A_{AL}1$ hydrolysis when the isomerization of the products is eliminated (see Table 4). In this way the activation parameters of *endo*-VI-OAc in Table 5 were estimated for these mechanisms.

The entropies of activation of the tertiary *exo* and tricyclic acetates are of the same order of magnitude as those of the tertiary monocyclic acetates but much more positive than those of the tertiary *endo* acetates (only the $A_{AL}1$ hydrolysis has been taken into account). This kind of large difference has not been found between *exo* and *endo* esters before.[4,8-10,18] The difference may be at least partly due to the contribution of the $A_{AC}2$ mechanism in the hydrolysis of *exo*-2-methyl-*endo*-2-norbornyl acetate (*endo*-II-OAc) and to the inaccuracy in the estimation of the activation parameters for the $A_{AL}1$ hydrolysis of *exo*-2-methyl-*endo*-2-norbornenyl acetate (*endo*-VI-OAc). The subject calls for further investigations.

The $A_{AC}2$ mechanism is characterized by the slight polar but large steric effects of an alkyl group.[15] The rates of hydrolysis of most secondary acetates in Table 5 are approximately equal. Thus they are sterically very much alike. The methyl substituents at the *exo*-2 position of *endo* acetates and at the *syn*-7 position of *exo* acetates have, however, a remarkable retarding effect in the $A_{AC}2$ hydrolysis. The great *exo*/*endo* rate ratios typical of the corresponding sulfonates[2-7] cannot be observed. Hydrolysis *via* carbonium ions (the $A_{AL}1$ mechanism) was expected for secondary *exo* and tricyclic acetates. However, the comparison of the hydrolysis rates of the secondary and the α-methyl substituted tertiary acetates (Table 5) with the solvolysis rates of the corresponding halides ($k_{tert}/k_{sec} \approx 10^4$)[23] implies that the proportion of the $A_{AL}1$ mechanism in the hydrolysis of the secondary acetates is negligible.

The $A_{AL}1$ mechanism is characterized by the slight steric but high polar influence of the alkyl group.[15] The rates of hydrolysis of the tertiary acetates differ quite remarkably from each other (Table 5). High *exo*/*endo* rate ratios (130 and 630 at 25 °C) typical of the corresponding saturated *p*-nitrobenzoates[9] are observed. The tertiary *exo* and tricyclic acetates hydrolyze faster and the tertiary *endo* acetates slower than 1-methylcyclohexyl (Hex-II-OAc) and tertiary butyl (*tert*-BuOAc) acetates, which cannot be explained by inductive effects only. 1-Methylcyclopentyl acetate (Pent-II-OAc), however, hydrolyzes at a rate which is of the same order of magnitude as those of *exo* acetates but much faster than those of *endo* acetates. This same pattern of reactivity in the uncatalyzed solvolyses of the corresponding chlorides[24] and *p*-nitrobenzoates[9,25,26] brought Brown to the conclusion that the *exo* esters (both secondary and tertiary) solvolyze at a "normal" rate but the *endo* isomers at a rate slower than "normal" by the S_N1 mechanism.[7] To find out whether the rates of hydrolysis of the tertiary *exo* and tricyclic acetates are higher or those of the tertiary *endo* acetates lower than "normal", the "normal" rates should be estimated.

Schleyer[27] calculated the "normal" relative rates of acetolysis for several secondary *p*-toluenesulfonates (tosylates) with reference to that of cyclohexyl tosylate using eqn. (4).

$$\log k_{rel} = (1715 - \nu_{CO})/8 + 1.32 \sum_{i}(1 + \cos 3\,\phi_i) + (GS - TS_{strain})/1.36 + (\text{inductive term}) \qquad (4)$$

The first term in the equation estimates the dependence of the rate of solvolysis on the angle strain at the reaction center (ν_{CO} is the carbonyl frequency in cm^{-1} of the ketone corresponding to the secondary alkyl group of the ester). The second term makes allowance for the torsional strains surrounding the reaction center (ϕ_i is a torsional angle). The third term is an estimate of the changes in the interactions between the nonbonded groups when proceeding from the initial state to the transition state, and the fourth term takes regard of the notable inductive factors.

Table 6. Estimation, by eqn. (5), of the rates of the $A_{AL}1$ hydrolyses for the tertiary acetates in a solution of 1.00 M perchloric acid in 60 wt. % dioxane-water at 25 °C.

Acetate	$0.152(1716-\nu_{CO})$	$1.43\sum_i(1+\cos 3\phi_i)$	$\frac{GS-TS_{strain}}{1.36}$	Ind. term.	log k_{rel} Calc.	Obs.
Hex-II-OAc	– (1716)[a]	–	0.6	–	0[b]	0[b]
Pent-II-OAc	−3.65(1740)	5.03	0.25	–	1.03[c]	1.03[c]
exo-II-OAc	−5.32(1751)	3.87	0.7	–	−1.35	1.92
endo-II-OAc	−5.32(»)	4.16	1.0	–	−0.76	−0.88
exo-VI-OAc	−4.41(1745)	3.87	0.3	−0.9	−1.74	0.71
endo-VI-OAc	−4.41(»)	4.16	0.5	−0.9	−1.25	−1.41
XI-OAc	−6.99(1762)	–	0.4	−0.5	−7.69	1.31

[a] Carbonyl frequency ν_{CO}/cm^{-1} of the ketone corresponding to the alkyl group of the acetate.[27] [b] Standard. [c] Calibration value.

Schleyer assumed when deriving eqn. (4) that all the solvolyses tested occur by the pure S_N1 mechanism.[27] However, it has been proved that the portion of the S_N2 mechanism (solvent assistance) in the solvolyses may be remarkable.[28] Therefore eqn. (4) is modified for the $A_{AL}1$ hydrolysis of the tertiary acetates by using the reference acetates available, Hex-II-OAc and Pent-II-OAc. The first three terms in the equation are re-estimated. When Schleyer determined the second term he used as the height of the rotational barrier the value 3.6 kcal/mol determined for ethyl chloride. This is here replaced by the value 3.9 kcal/mol determined for isopropyl chloride (a mean of 3.45 and 4.32 kcal/mol).[29,30] Thus the torsional strains caused by the α-methyl group are also taken into account. In the case of bicyclic compounds the torsional angles are obtained from the results of Altona and Sundaralingam,[31] otherwise the angles proposed by Schleyer have been accepted. The nonbonded interactions of the third term are calculated by using results of equilibrations and estimations reported by several authors (the more detailed treatment is in Ref. 1).[19,20,27,32–35] The coefficient of the first term is obtained in the way that the sum of the second and third terms is subtracted from the logarithm of the observed relative (to Hex-II-OAc) rate of hydrolysis of the reference acetates (see Table 6) and the results are plotted *versus* $1716-\nu_{CO}$. In this way the approximate eqn. (5) is obtained for the "normal" hydrolysis rates of the tertiary acetates when, besides, it is assumed that the energies

$$\log k_{rel} = 0.152(1716-\nu_{CO}) + 1.43\sum_i(1+\cos 3\phi_i) + (GS-TS_{strain})/1.36 + (\text{inductive term}) - 0.60 \quad (5)$$

calculated above are negligible in the transition state. The calculated and observed relative rates of hydrolysis are collected in Table 6. Results should be considered quite semiquantitative due to the fact that only two reference acetates were used when determining the coefficient of the first term.

According to Table 6 the observed rates of hydrolysis for the tertiary *exo* acetates (*exo*-II-OAc and *exo*-VI-OAc) are 2 – 3 powers of ten greater than estimated for the unassisted hydrolysis. This agrees with the deductions of Winstein [2] and Paasivirta [36] that *endo*-2-methyl substituted 2-norbornyl and 2-norbornenyl esters (and alcohols) solvolyze *via* nonclassical [2] or seminonclassical [36,37] transition states. The observed rate of hydrolysis for 3-methyl-3-nortricyclyl acetate (XI-OAc) is about nine powers of ten greater than estimated, which result is in agreement with the powerful participation of the three-membered carbon ring.[3,5,38] The anchimeric assistances, *i.e.* log k_{rel} (obs) – log k_{rel} (calc), evaluated in this work are within *ca.* one logarithmic unit equal to those estimated for the acetolysis of the corresponding secondary tosylates.[27] The observed rates of hydrolysis for the tertiary *endo* acetates (*endo*-II-OAc and *endo*-VI-OAc) are nearly equal to the estimated rates, which observation is similar to that made by Schleyer for the acetolysis of

the corresponding secondary tosylates.[37] The *endo*-6 hydrogen in the saturated skeleton and the *endo*-π orbital of the homoallylic double bond do not seem to have a considerable hindering effect on the departure of acetic acid from the *endo*-2 position (*cf.* Refs. 7 – 10, 13, 36).

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REFERENCES

1. Lajunen, M. *Kinetics and Product Analyses of the Acid-Catalyzed Hydrolyses of Some Secondary and Tertiary 2-Norbornyl, 2-Norbornenyl, and 3-Nortricyclyl Acetates*, Diss., University of Turku, Turku 1973.
2. Winstein, S. *J. Amer. Chem. Soc. 87* (1965) 381, with refs.
3. Roberts, J. D. and Bennett, W. *J. Amer. Chem. Soc. 76* (1954) 4623.
4. Berson, J. A. In de Mayo, P., Ed., *Molecular Rearrangements*, Interscience, London 1963, Chapter 3, with refs.
5. Capon, B. *Quart. Rev. Chem. Soc. 18* (1964) 45, with refs.
6. Sargent, G. D. *Quart. Rev. Chem. Soc. 20* (1966) 301, with refs.
7. Brown, H. C. a. *Chem. Brit. 2* (1966) 199; b. *Chem. Eng. News 45* (Feb. 13, 1967) 87; c. *Accounts Chem. Res. 6* (1973) 377, with refs.
8. Brown, H. C. and Ikegami, S. *J. Amer. Chem. Soc. 90* (1968) 7122.
9. Ikegami, S., Vander Jagt, D. L. and Brown, H. C. *J. Amer. Chem. Soc. 90* (1968) 7124, with refs.
10. Peters, E. N. and Brown, H. C. *J. Amer. Chem. Soc.* a. *94* (1972) 5899, 7920; b. *95* (1973) 2397, 2398.
11. Jensen, F. R. and Smart, B. E. *J. Amer. Chem. Soc. 91* (1969) 5686, 5688.
12. Bunton, C. A., Khaleeluddin, K. and Whittaker, D. *J. Chem. Soc.* (1965) 3290.
13. Bunton, C. A., O'Connor, C. and Whittaker, D. *J. Org. Chem. 32* (1967) 2812.
14. Radhakrishnamurti, P. S. and Patra, P. C. *Proc. Indian Acad. Sci. A 71* (1970) 181.
15. Euranto, E. K. In Patai, S., Ed., *The Chemistry of Carboxylic Acids and Esters*, Interscience, London 1969, pp. 549 – 569.
16. Paasivirta, J. and Äyräs, P. *Suom. Kemistilehti B 41* (1968) 51.
17. Alberty, R. A. and Miller, W. G. *J. Chem. Phys. 26* (1957) 1231, with refs.
18. McDaniel, D. H. and Brown, H. C. *J. Org. Chem. 23* (1958) 420.
19. Rei, M.-H. and Brown, H. C. *J. Amer. Chem. Soc. 88* (1966) 5335.
20. Hirsjärvi, P., Kauppinen, H.-L. and Paavolainen, S. *Suom. Kemistilehti B 42* (1969) 236.
21. Winstein, S., Clippinger, E., Howe, R. and Vogelfanger, E. *J. Amer. Chem. Soc. 87* (1965) 376.
22. Bunton, C. A. and Shiner, V. J. *J. Amer. Chem. Soc. 83* (1961) 3207, with refs.
23. Fry, J. L., Harris, J. M., Bingham, R. C. and Schleyer, P. v. R. *J. Amer. Chem. Soc. 92* (1970) 2540.
24. Brown, H. C. and Rei, M.-H. *J. Amer. Chem. Soc. 86* (1964) 5008.
25. Brown, H. C. and Dickason, W. C. *J. Amer. Chem. Soc. 91* (1969) 1226.
26. Fort, R. C., Hornish, R. E. and Liang, G. A. *J. Amer. Chem. Soc. 92* (1970) 7558.
27. Schleyer, P. v. R. *J. Amer. Chem. Soc. 86* (1964) 1854, 1856.
28. Fry, J. L., Lancelot, C. J., Lam, L. K. M., Harris, J. M., Bingham, R. C., Raber, D. J., Hall, R. E. and Schleyer, P. v. R. *J. Amer. Chem. Soc. 92* (1970) 2538.
29. Tobiason, F. L. and Schwendeman, R. H. *J. Chem. Phys. 40* (1964) 1014.
30. Möller, K. D., De Meo, A. R., Smith, D. R. and London, L. H. *J. Chem. Phys. 47* (1967) 2609.
31. Altona, C. and Sundaralingam, M. *J. Amer. Chem. Soc. 92* (1970) 1995.
32. Eliel, E. L., Allinger, N. L., Angyal, S. J. and Morrison, G. A. *Conformational Analysis*, Wiley, New York 1965, pp. 44, 51, 202.
33. Wilcox, C. F., Sexton, M. and Wilcox, M. F. *J. Org. Chem. 28* (1963) 1079.
34. Goering, H. L. and Schewene, C. B. *J. Amer. Chem. Soc. 87* (1965) 3516.
35. Ouellette, R. J., Rawn, J. D. and Jreissaty, S. N. *J. Amer. Chem. Soc. 93* (1971) 7117.
36. Paasivirta, J. a. *Justus Liebigs. Ann. Chem. 686* (1965) 1; b. *Acta Chem. Scand. 22* (1968) 2200.
37. Olah, G. A., White, A. M., DeMember, J. R., Commeyras, A. and Lui, C. Y. *J. Amer. Chem. Soc. 92* (1970) 4627.
38. Olah, G. A. and Liang, G. *J. Amer. Chem. Soc. 95* (1973) 3792.

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