300. The Cyclopropylcarbinyl-Cyclobutyl-Homoallylic Rearrangement. Part III. Evidence for a Symmetrical Intermediate and for Two Discrete Rearrangement Processes

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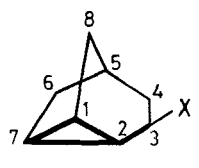
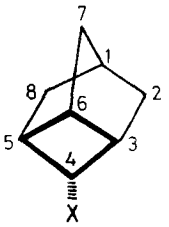
Summary. In buffered 70% aqueous dioxane the cyclopropylcarbinyl (**1**-X), *endo*-cyclobutyl (**2**-X) and homoallylic (**3**-X) derivatives (X = nucleofuge) react to give the same mixture of alcohols **1**-OH and **3**-OH by way of a common intermediate, the symmetrical homoallylic ion **22**. This follows from a study of optically active reactants **1**-X and **3**-X and from the deuterium scrambling pattern in the products from deuteriated **1**-X, *endo*-**2**-X and **3**-X. The high solvolysis rates of **3**-X indicate π-bond participation in the transition state, while the high rates of **1**-X and *endo*-**2**-X reflect strong σ-bond participation which is absent in *exo*-**2**-X.

Prolonged heating of **1**-X, *endo*-**2**-X and **3**-X in formic acid leads to a degenerate rearrangement of the initially formed **3**-formate. As evidenced by deuterium scrambling, carbon atoms 1, 3 and 7 eventually become positionally equivalent in the latter compound.

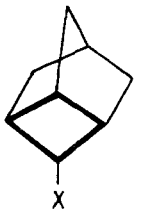
1. Introduction. – The interconversion of cyclopropylcarbinyl-, cyclobutyl- and homoallylic derivatives[1a]), such as the compounds **1**, *endo*- and *exo*-**2** and **3** (X = nucleofuge) in solvolytic reactions has continued to attract widespread attention. As is evident from recent review articles [1] research in this area has tended to concentrate on the still controversial nature and number of intermediates involved in the rearrangements[2]).



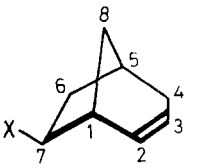
1-X



endo-**2**-X



exo-**2**-X



3-X

In Part I [3] the preparation of the four isomeric secondary alcohols tricyclo[3.2.1.$0^{2,7}$]octan-3-ol (**1**-OH), *endo*- and *exo*-tricyclo[3.2.1.$0^{3,6}$]octan-4-ol (**2**-OH) and *exo*-bicyclo[3.2.1]oct-2-en-7-ol (**3**-OH) was described. These compounds were selected as models for a detailed study of the CCH-rearrangement because the relevant

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[1]) Author, to whom correspondence should be addressed.

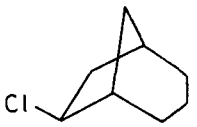
[1a]) Abbreviated as CCH-rearrangement.

[2]) The nature of the intermediates under non-nucleophilic, *i.e.* stable ion conditions, has been studied by *Olah et al.* [2] and others [1]. As stressed by these authors the observed carbocations are not necessarily identical with the intermediates in solvolytic reactions.

units of four carbon atoms[3]) are held together in a rigid arrangement of defined geometry by four additional carbon atoms. This reduces the stereochemical uncertainities which are present in mobile molecules.

In Part II [4] the reaction products and rates of the 2,4-dinitrobenzoates (X = O*Dnb*) of the isomeric alcohols in 70% aqueous dioxane, buffered with triethylamine, were reported. All three esters lead to the same mixture (± 1%) consisting of 78% cyclopropylmethanol **1**-OH and 22% homoallylic alcohol **3**-OH. A common cationic intermediate was therefore implicated in these kinetically controlled reactions. On the other hand reaction in formic acid lead to the most stable product, *i.e.* the formate of the homoallylic alcohol **3**-OH.

Furthermore, in 70% dioxane **1**-O*Dnb* and *endo*-**2**-O*Dnb* reacted 7.2×10^3 and 7.7 times, respectively, as fast as the homoallylic isomer **3**-O*Dnb*. Since the corresponding chloride **3**-Cl reacted *ca.* 2×10^5 faster than the saturated analogue, *i.e.* 7-*exo*-bicyclo[3.2.1]octyl chloride (**4**), all three esters show large rate enhancements. On the other hand *exo*-**2**-O*Dnb* reacted more slowly than the *endo*-isomer and solvolysis was accompanied by ester hydrolysis to *exo*-**2**-OH.



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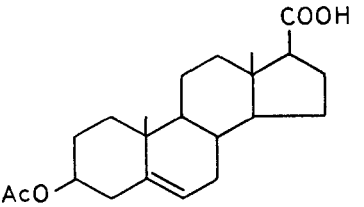

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While these results are typical of these compounds, they shed no light on the nature and number of intermediates involved in the CCH-rearrangements. Clearly, these questions can only be resolved by employing more sensitive probes, *e.g.* by the use of optically active or isotopically labeled starting materials. Such studies have now been carried out[4]) and the present paper deals with the preparation and solvolysis of optically active esters, *i.e.* the *p*-nitrobenzoate **1**-O*Pnb* and the 2,4-dinitrobenzoate **3**-O*Dnb*, as well as the deuterium labeled esters **1**-O*Pnb*-3-*d*, endo-**2**-O*Dnb*-3,5-d_2 and 4-*d* and **3**-O*Dnb*-7-*d*[5]).

Solvolyses were carried out in 70% aqueous dioxane and in formic acid, *i.e.* in a strongly nucleophilic solvent and in a weakly nucleophilic solvent of high ionizing power. As mentioned above *exo*-**2**-O*Dnb* is less reactive than its *endo*-isomer by an as yet unknown factor. This question has now been resolved by measuring the solvolysis rates of the epimeric methanesulfonates *endo*- and *exo*-**2**-OMs. The results of these studies are discussed in Section 3[6]).

2. Results. – The racemic alcohols **1**-OH and **3**-OH[7]) were resolved by fractional crystallization of their esters with 3β-acetoxy-Δ^5-etiocholenic acid (**5**) [5], which

[3]) These are connected by heavy lines in the formulae.

[4]) Previous studies employing these techniques have been reviewed [1].

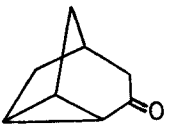
[5]) The numerals followed by *d* for deuterium indicate its position in the starting material.

[6]) Preliminary results of these studies have been reported briefly [6].

[7]) *endo*- and *exo*-**2**-OH possess a plane of symmetry.

proved to be the best resolving agent for these highly reactive compounds. Reductive ester cleavage with $LiAlH_4$ led to the optically active alcohols **1**-OH and **3**-OH. The former was converted to the *p*-nitrobenzoate **1**-O*Pnb* ($[\alpha]_D = -71°$), the latter to the 2,4-dinitrobenzoate **3**-O*Dnb* ($[\alpha]_D = 31.4°$,$CHCl_3$).

Upon reaction in 70% dioxane, buffered with triethylamine, the ester **1**-O*Pnb* yielded a mixture of optically *inactive* **1**-OH (72.5%), **3**-OH (14.5%) and the corresponding *p*-nitrobenzoate **3**-O*Pnb* (13%). The latter compound is evidently formed by ion pair recombination. In fact the ratio of the first order rate constants for loss of optical activity at 60.0° ($k_\alpha = 6.22 \times 10^{-4}$ s^{-1}) and the conductometric rate constant ($k_c = 4.1 \times 10^{-4}$ s^{-1}) in 70% dioxane indicates an ion pair return factor of 1.5. Likewise, the optically active ester **3**-O*Dnb* led to a mixture of *inactive* **1**-OH (82%) and **3**-OH (18%). In this case the ratio of k_α (3.35×10^{-5}) and k_c (2.19×10^{-5}) was 1.53 at 90.0°. Finally, a control experiment showed that optically active **1**-OH is not racemized under the reaction conditions.



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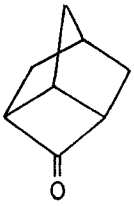

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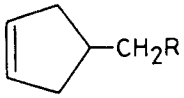
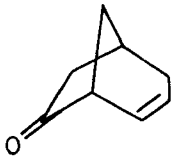


8 R =

a COOH
b COCl
c $COCDN_2$
d CD=C=O

Tricyclo[3.2.1.$0^{2,7}$]octan-3-ol (**1**-OH) deuteriated at C(3), *i.e.* **1**-OH-3-*d*, was prepared by reduction of the ketone **6** [3] with $LiAlD_4$ and converted to the *p*-nitrobenzoate **1**-O*Pnb*-3-*d*. *endo*- and *exo*-**2**-OH-4-*d* were obtained in the same way from the ketone **7** [3]. The deuteriated epimeric alcohols were separated by chromatography and the *endo*-isomer converted to the 2,4-dinitrobenzoate *endo*-**2**-O*Dnb*-4-*d*. The absence of hydrogen at C(3) and C(4) respectively, in the two esters was confirmed by their ^{1}H-NMR. spectra.

Deuterium was introduced at C(3) and C(5) of the *endo*-alcohol **2**-OH by converting the acid chloride **8b** of cyclopenten-3-yl acetic acid **8a** to the diazoketone **8c** with deuterio-diazomethane. The latter was photochemically rearranged to the ketene **8d**, the precursor of the ketone **7** [3]. For reasons of symmetry the deuterium in **8d** must be equally distributed between C(3) and C(5) of the ketone **7**. Reduction of the latter with $LiAlH_4$ led to *endo*- and *exo*-**2**-OH-3,5-d_2. The *endo*-alcohol was converted to the 2,4-dinitrobenzoate *endo*-**2**-O*Dnb*-3,5-d_2, the total amount of deuterium incorporated being 88%±2%, as determined by ^{1}H-NMR. spectroscopy.



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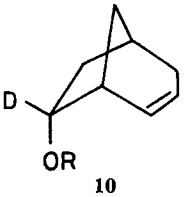

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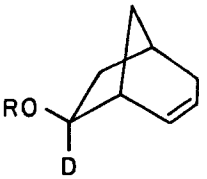
a R = H
b R = *o*-$BrC_6H_4SO_2$
c R = CH_3CO



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Deuterium was introduced at C(7) of **3**-OH by a circuitous route which was first tried out with undeuteriated material. *exo*-**3**-OH was oxidized to the ketone **9** with silver carbonate. The ketone was then reduced to the *endo* alcohol **10a**-7-*d* with $LiAlD_4$ in 98% yield. The *p*-bromobenzenesulfonate **10b** underwent a displacement reaction with tetra(*n*-butyl)-ammonium acetate in dry benzene yielding the *exo*-acetate **11c**-7-*d*. Upon reductive cleavage with $LiAlH_4$ the latter afforded *exo*-**3**-OH-7-*d*. The ^{1}H-NMR. spectrum of the deuteriated 2,4-dinitro-benzoate **3**-O*Dnb*-7-*d* revealed the presence of 93 $\pm$1% deuterium at C(7).

The solvolyses of the deuteriated esters of **1**-OH, *endo*-**2**-OH and **3**-OH in buffered 70% dioxane were carried out as previously described [4]. The distribution of deuterium in the resulting alcohols **1**-OH and **3**-OH was determined by comparison of their 100-MHz-^{1}H-NMR. spectra with those of the undeuteriated compounds, account being taken of the total deuterium content of the starting material. In order to obtain a better separation of the ^{1}H-NMR. signals, the spectra were usually measured in the presence of the chemical shift reagent Eu(fod)$_3$, as previously described [3]. An analysis of the results of several integrations of relevant signals revealed an accuracy of $\pm$ 2 to 4%. The deuterium distributions observed are listed in Table 1.

Table 1. *Deuterium distribution in the solvolysis products of deuteriated esters in 70% dioxane and formic acid*

ester	solvent	% deuterium in products	
		1-OH	**3**-OH[a]
1-O*Pnb*-3-*d*	70% dioxane	C(3) 100	C(3) 100
	HCOOH[a]		C(1) 33
			C(3) 29
			C(7) 37
endo-**2**-O*Dnb*-4-*d*	70% dioxane	C(2) 100	C(2) 100
	HCOOH		C(2) 100
endo-**2**-O*Dnb*-3,5-d_2[b]	70% dioxane	C(1) 26	
		C(7) 23	
		C(3) 51	
	HCOOH		C(1) 33
			C(3) 32
			C(7) 35
3-O*Dnb*-7-*d*	70% dioxane	C(1) 46	[c] C(1) 50
		C(7) 54	[c] C(7) 50
	HCOOH		C(1) 33
			C(3) 31
			C(7) 36

[a] Formolysis products isolated and measured as the 7-formate.
[b] Containing 50% deuterium at each C(3) and C(5).
[c] Percentage approximate due to small sample size.

Formolysis of the three deuteriated esters in Table 1 led to **3**-formate in which the deuterium was scrambled among three positions C(1), C(3) and C(7). In this case the signals of the remaining protons at these carbon atoms were incompletly separated even in the presence of $Eu(fod)_3$. Because of the resulting inaccuracy of the proton integrations ($\pm$ 5–7%) resort was taken to 13.81-MHz-^{2}H-NMR. spectroscopy which permits the distribution of deuterium at C(1), C(3) and C(7) to be determined directly by integration of the corresponding deuterium signals with an accuracy of $\pm$ 2–3%. The degree of scrambling increased with time until the deuterium was equally distributed among C(1), C(3) and C(7) (Table 1). At 50° this required 24–40 hours. It is noteworthy that in 1 *N* H_2SO_4 in 70% dioxane the alcohol *endo*-**2**-OH-3,5-d_2 rearranges quantitatively to **3**-OH containing *ca.* 25% deuterium at C(1) and C(7) and *ca.* 50% at C(3), *i.e.* the same scrambling is observed as for the 2,4-dinitrobenzoate in buffered 70% dioxane.

The first order rate constants for the methanesulfonates of *endo*- and *exo*-**2**-OH in ethanol at three temparatures are listed in Table 2 together with their activation parameters. At 80.0° the extremely unstable *endo*-**2**-OMs reacts 5.14×10^5 times faster than the *exo*-isomer. In 70% dioxane *exo*-**2**-OMs yielded 81% **1**-OH and 19% **3**-OH. The corresponding *p*-toluenesulfonate *exo*-**2**-OTs led to 78.5% **1**-OH and 21.5% **3**-OH. These yields are very close to those obtained with *endo*-**2**-O*Dnb*, **1**-O*Pnb* and **3**-O*Dnb* and suggest a common cationic intermediate and only a minor influence of the counter ion.

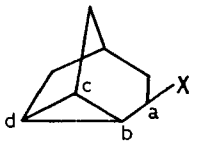
Table 2. *First order rate constants for* endo- *and* exo-**2**-*OMs in dry ethanol with 2 equiv. of triethylamine*

	T (°C)	k (s^{-1})	$H^{\neq}$ kcal/mol	$S^{\neq}$ cal/mol degree
endo-**2**-OMs	0.00	5.45×10^{-4}		
	10.00	2.14×10^{-3}		
	20.00	7.81×10^{-3}		
	80.00 [a])	3.75	20.47	1.8
exo-**2**-OMs	80.00	7.30×10^{-6}	25.73	−9.5
	90.00	2.07×10^{-5}		
	100.00	5.50×10^{-5}		

[a]) Extrapolated.

3. Discussion. – The results reported in this and the previous paper [4] clearly show that different processes occur in 70% aqueous dioxane and in formic acid, respectively. In the former solvent the three 2,4-dinitrobenzoates of **1**, **2** and **3** afford the same mixture of alcohols **1**-OH and **3**-OH, whereas in formic acid only the formate of the most stable product **3**-OH is formed. The former reaction is therefore subject to kinetic control, the latter to thermodynamic control. The nature of the two processes is clearly revealed by the speed and the pattern of deuterium scrambling in the resulting products. The process occuring in aqueous dioxane will be discussed first.

The formation of the same mixture of racemic **1**-OH and **3**-OH upon solvolysis of optically active **1**-O*Pnb* and **3**-O*Dnb* demonstrates that products are formed by way of a symmetrical intermediate. This also applies to the initially formed ion pair from **1**-O*Pnb* since its internal recombination product, **3**-O*Pnb*, is also racemized. The symmetry of the intermediate also follows from the location of the deuterium in the alcohols **1**-OH and **3**-OH obtained from labeled reactants (Table 1)[8].



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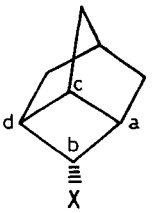
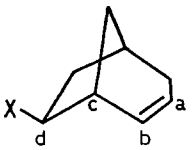


endo-**2**



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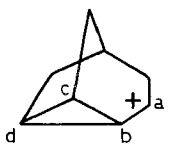
Thus, within the limits of the accuracy of the method employed, deuterium at *a* in the reactant **1**-O*Pnb* is still located at *a* in the products **1**-OH and **3**-OH; therefore no position becomes equivalent to *a* in the intermediate. Likewise, deuterium at *b* in **2**-O*Dnb* remains at *b* in **1**-OH and **3**-OH, hence no other carbon atom becomes equivalent to *b* in the intermediate. On the other hand, deuterium at *d* in **3**-O*Dnb* is distributed equally between *c* and *d* in the products **1**-OH and **3**-OH. These positions therefore become equivalent in the intermediate. This is confirmed by the solvolysis of *endo*-**2**-O*Dnb* containing equal amounts of deuterium at the equivalent positions *a* and *d*. In the product **1**-OH half of the deuterium is equally partitioned between *c* and *d* while the other half is still located at *a*.



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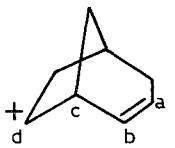

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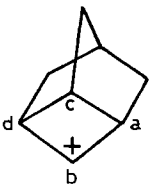

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These results are compatible with an intermediate possessing a plane of symmetry through the carbon atoms *a* and *b* and which bisects the *c*-*d* bond, as in the cyclopropylcarbinyl part of ion **12** or, alternatively, with a rapid equilibrium between **12** and the homoallylic ion **13**. On the other hand the cyclobutyl ion **14** does not qualify as an intermediate for the reaction of *endo*-**2**-O*Dnb*, because carbon atoms *a* and *d* should then become equivalent. However, equilibration of ordinary carbenium ions, *i.e.* **12**, **13**, **14**, is also excluded for other reasons.

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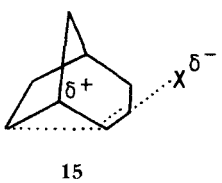
[8] In order to avoid confusion due to the different numbering of the Carbon atoms in **1** and **3** on the one hand and in **2** on the other, the relevant atoms are marked by small letters in the following formulae.



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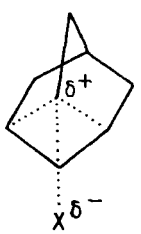

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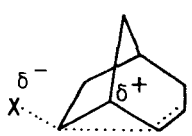

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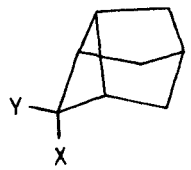

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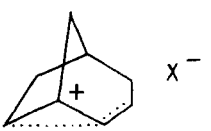
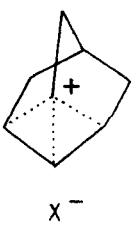
a X = OMs, Y = H
b X = H, Y = OMs

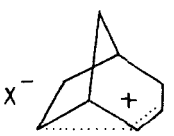
Thus, it is generally agreed that ionization is assisted by delocalization of the strained σ-bonds in cyclopropylcarbinyl and cyclobutyl derivatives and by π-bond delocalization in homoallylic derivatives [1]. This follows from the greatly enhanced solvolysis rates of molecules of this type. These effects are illustrated in the descriptions **15**, **16** and **17** of the transition states for the ionization of **1**-X, *endo*-**2**-X and **3**-X, respectively. In **15** the bent *b-d* bond is most nearly antiplanar to the *a*-X bond. In *endo*-**16**-X both the bent *a-c* and *d-c* bonds meet this requirement, as pictured in **18a**. In *exo*-**2**-OMs (**18b**), which reacts *ca.* 5×10^5 more slowly than the *endo*-isomer[9]), there is no strained σ-bond properly aligned to assist ionization; therefore initial formation of an ordinary cyclobutyl cation **14** is indicated. Finally, in **3**-X the π-orbital of the double bond is suitably orientated to assist ionization as depicted in the transition state **17**.



19



20



21

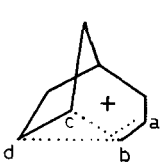
Further separation of the nucleofuge X in **15**, **16** and **17** should lead to the ion pairs **19**, **20** and **21**, respectively[10]). **19** and **21** are identical unsymmetrical homoallylic ions [8] which differ only with respect to the location of the counter ion X^-. The cation in **20**, however, represents a symmetrical bicyclobutonium ion [9]. Since none of these cations explain the results obtained with optically active and deuterium labeled reactants they must pass rapidly into the symmetrical homoallylic cation **22** [8b] [10][11]). This requires very little movements of atoms in the ions

[9]) A rate ratio of this order of magnitude was observed by *Wiberg* & *Hess* [7] for *endo*- and *exo*-6-bicyclo[3.1.1]heptyl tosylate.

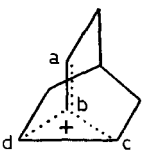
[10]) The dotted-line symbols have the merit, not shared by the solid-line symbols **12**, **13** and **14**, of expressing the considerable electron delocalization in these ions.

[11]) These are also called bisected cyclopropylcarbinyl cations [1b]. It is of course recognized that unsymmetrical homoallylic cations might be more stable in stereochemically constrained molecules, *cf.* [11].

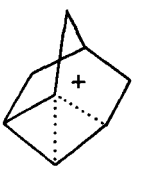
19 and **21**, considerably more in the case of **20**. The question whether the latter ion is a true intermediate or represents a later stage in the activation process leading to **22** remains unresolved. It should also be added that neither the unsymmetrical bicyclobutonium ion **23** [12] nor the tricyclobutonium ion **24** [13] can explain the results as does the symmetrical cation **22**, also depicted as **22a**[12]). Thus attack of water from both sides at *a* yields racemic **1**-OH, while attack at the equivalent carbon atoms *c* and *d* yields racemic alcohol **3**-OH. Evidently attack at *b* in **22** (or **20**) to yield **2**-OH does not compete successfully.



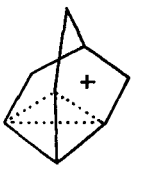
22



22a

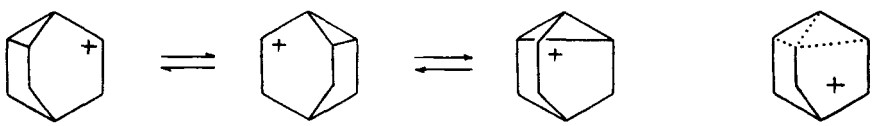


23



24

The reactions discussed so far were carried out in aqueous dioxane buffered with triethylamine. Without base or in the presence of 1 N H_2SO_4 the alcohols **1**-OH and **2**-OH rearranged rapidly to the more stable **3**-OH. As shown with *endo*-**2**-O*Dnb*-3,5-*d* the deuterium scrambling pattern indicates the intermediacy of the same symmetrical homoallylic ion **22**. However, when the deuteriated esters **1**-O*Pnb*, *endo*-**2**-O*Dnb* and **3**-O*Dnb* were subjected to prolonged heating in formic acid scrambling in the resulting formate **3**-OCHO increased until the deuterium was equally distributed among the positions *a*, *c* and *d*. Only position *b* remained unaffected and did not acquire deuterium (Table **1**). Again, no intermediate having the symmetry of the cyclobutyl cation **14** or **20** was formed. Since the structure of the formate **3**-OCHO is not altered in this reaction, while the carbon atoms *a*, *c* and *d* become equivalent, the process represents a degenerate rearrangement [15]. Apparently, repeated generation of the symmetrical homoallylic ion **22** allows it to undergo the isomerization process **25a** $\rightleftarrows$ **25b** $\rightleftarrows$ **25c**[13]), which is favored by the low nucleophilicity and high ionizing power of formic acid.



25a **25b** **25c** **26**

Degenerate CCH-rearrangements have been detected before with the aid of deuterium- and ^{14}C-labeling [9b] [12] [13] [16] [17][14]). However, positional scrambling was incomplete in these cases, apparently because capture of the initial intermediate by solvent competed with its further degenerate rearrangement. These two

12) This type of symmetrical intermediate has been favored in several previous studies of the CCH-rearrangement [9b] [14].

13) Another view of **22** and solid-lined bonds are shown for the sake of clarity.

14) It has been directly observed under stable ion conditions [2].

discrete processes have been separated in this study by using appropriate solvents. Degenerate CCH-rearrangements are known to occur with high stereoselectivity [17] [18] and symmetrical bicyclobutonium ions of the structure **26** are likely transition states [9].

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Experimental Part

Melting points were determined on a *Kofler-Block* and are corrected. IR. spectra in cm^{-1}, ^1H-NMR. spectra in δ-values (ppm). Gas-Chromatography (GLC.) analyses were carried out employing columns packed with A) 10% carbowax 20M on chromosorb W; B) 20% carbowax 20M on chromosorb G.

1. Preparation of the optically active alcohols *1*-OH and *3*-OH. – 1.1. *Optically active tricyclo[3.2.1.0^{2,7}]octan-3-ol* (**1**-OH). Following a known procedure [5] 17.3 g (48 mmol) 3β-acetoxy-Δ^5-etiocholenic acid (**5**) (m.p. 235–242°, $[\alpha]_D = -29°$, $CHCl_3$) were stirred with 100 g pure thionyl chloride for 4 h at 22°. Excess $SOCl_2$ was removed in a vacuum rotary evaporator (VRE.) at 80°. After drying at 22° i.V. the crystalline acid chloride was dissolved in 150 ml dry pyridine and a cold solution of 5.37 g (43.2 mmol) rac. **1**-OH in 50 ml dry pyridine was added at 0° during 5 min. After 24 h at 22° the solution was slowly poured into a mixture of 180 ml conc. hydrochloric acid, 950 ml ice water and 1 l of ether. After shaking the mixture was filtered and the water layer separated. The latter was twice extracted with 750 ml ether. The combined ether extracts were washed with 50 ml of aqueous 10% $NaHCO_3$-solution, repeatedly with distilled water, dried over Na_2SO_4 and evaporated to dryness in a VRE. The brown viscous residue, 18.6 g, was chromatographed on 150 g silica gel with benzene. Removal of the benzene fractions in a VRE. yielded 13.9 g (69%) of lightly colored oil, which crystallized spontaneously. After two recrystallizations from *n*-hexane 2.72 g needles, m.p. 136–151°; $[\alpha]_D = -62.4°$ ($c = 1.27$, $CHCl_3$). This material was used for the racemizations described below. A small sample was recrystallized to constant rotation $[\alpha]_D = -75°$ ($c = 1.0$, $CHCl_3$), m.p. 161–167°. – IR. (CCl_4): 3045 (cyclopropyl); 1726 (C=O).

$C_{30}H_{42}O_4$ (466.67) Calc. C 77.21 H 9.07% Found C 76.98 H 9.21%

1.00 g (2.15 mmol) of the above ester of **5** with **1**-OH $[\alpha]_D = -62.4°$ ($c = 1.27$, $CHCl_3$) in 120 ml dry ether was added to 0.596 g (15.7 mmol) $LiAlH_4$ in 100 ml dry ether during 30 min with vigorous stirring. After further 3.5 h 2.4 ml of 4% aqueous NaOH-solution were added at 0° and the resulting precipitate filtered off. The latter was washed with ether and the combined ether solutions were distilled through a *Vigreux* column. The crystalline residue was taken up in pentane, the solution filtered, concentrated to 2 ml and transferred to sublimation apparatus. Careful sublimation at 80°/11 Torr yielded 237 mg (89%) of volatile crystals, $[\alpha]_D = -51°$ ($c = 0.89$, $CHCl_3$). GLC. analysis on column A revealed material of 97% purity identical to **1**-OH beside *ca.* 3% of rearranged **3**-OH.

p-*Nitrobenzoate of optically active* **1**-*OH*. This was prepared according to the procedure described for inactive **1**-O*Pnb* [3] starting with **1**-OH ($[\alpha]_D = -51°$). Yield 388 mg (84%). From *n*-hexane 250 mg (54%), m.p. 79.5–81.5°, $[\alpha]_D = -71.2°$ ($c = 0.46$, $CHCl_3$). – IR. and NMR. were the same as for inactive material [3].

$C_{15}H_{15}NO_4$ (273.29) Calc. C 65.92 H 5.53 N 5.13% Found C 66.22 H 5.72 N 5.17%

1.2. *Optically active* exo-*bicyclo[3.2.1]oct-2-en-7-ol* (**3**-*OH*). Resolution of rac. **3**-OH was carried out as described under 1. The acid chloride from 31.8 g (88.3 mmol) of **5** was reacted with 10.95 g (88 mmol) of alcohol **3**-OH [3] to yield, after chromatography on 120 g silica gel, 27.47 g (67%) of crystalline ester. Four crystallizations from *n*-hexane afforded 2.99 g, $[\alpha]_D = -1.7°$ ($c = 0.66$, $CHCl_3$), m.p. 160–164°. Reductive cleavage of this material with 1.83 g (4.83 mmol) $LiAlH_4$ and sublimation of the crude product at 80°/11 Torr yielded 728 mg (94.6%) active **3**-OH, $[\alpha]_D = 61°$ ($c = 0.66$, $CHCl_3$), m.p. 38–48°.

The 2,4-dinitrobenzoate of optically active **3**-OH was prepared as described [3]. From *n*-hexane m.p. 99–101°, $[\alpha]_D = 31.4°$ ($c = 0.61$, $CHCl_3$), yield 67%. – IR. (CCl_4): 3040 (vinyl CH); 1735 (C=O); 1536, 1350 (NO_2), identical with rac. **3**-O*Dnb* [3].

2. Deuteriated compounds. – 2.1. 7-[^2H]-exo-*Bicyclo[3.2.1]oct-2-en-7-ol* (**3**-OH-7-*d*). *Bicyclo[3.2.1]oct-2-en-7-one* (**9**). 1.56 g (12.6 mmol) **3**-OH were heated under reflux with 78 g freshly prepared silver carbonatecellite [19] in 375 ml dry benzene. The oily residue, obtained after filtration and removal of solvent in a VRE., was glass-bulb distilled at 100°/11 Torr to yield 1.35 g of colorless, very hygroscopic oil (**9**). $n_D^{25} = 1.5007$. – IR. (CS_2): 3030, 690 (*cis*-olefin); 1740 (C=O). UV. (cyclohexane): λ_{max} 199.5 (log ε 3.852); 284.5 (log ε 2.281); 292.5 (log ε 2.360); 302.5 (log ε 2.32); 313 (log ε 2.04).

The *2,4-dinitrophenylhydrazone*, from aqueous ethanol, yielded light-red needles, m.p. 150–151.5°.

$C_{14}H_{14}N_4O_4$ (302.30) Calc. C 55.62 H 4.67 N 18.54% Found C 55.47 H 4.81 N 18 55%

endo-*Bicyclo[3.2.1]oct-2-en-7-ol* (**10a**) *and* 7-[^2H]-**10a** (**10a**-7-d). 930 mg (7.6 mmol) ketone **9** in 140 ml dry ether were reduced with 464 mg (12.2 mmol) $LiAlH_4$ and $LiAlD_4$, respectively, for 8 h at 22°. 1.84 ml 4% aqueous NaOH were added, the mixture filtered and washed with ether. Evaporation of the ether extracts yielded a crystalline residue; after sublimation at 80°/11 Torr 847 mg (90%), m.p. 71–75°. GLC. revealed the presence of *ca.* 2% *exo*-**3**-OH. – IR. (CCl_4): 3635 (OH free); 3590 (OH intramolecular assoc.); 3040 and 675 (*cis* olefin); 1403, 1129 and 1072. – NMR. (CCl_4): 0.8–2.7 (*m*, 9H); 4.0–4.5 (*m*, 1H, H—C(7)). This signal is missing in the spectrum of **10a**-7-*d*); 5.35–5.90 (*m*, 2H, vinyl H).

p-*Bromobenzenesulfonate of* **10a** *and* **10a**-7-d. 7.47 mg (5.98 mmol) of **10a** were reacted with 1.74 g (6.83 mmol) *p*-bromobenzenesulfonyl chloride for 12 h at 22°. After addition of 14 ml water the mixture was extracted 3 times with each 35 ml $CHCl_3$. The extracts were washed with cold aqueous 2N HCl and water, dried over Na_2SO_4 and evaporated in a VRE. at 40°. From *n*-hexane 1.69 g **10b** (82.5%), m.p. 72–74°. – IR. (CCl_4): 3040 (vinyl CH); 1376 and 1188 (SO_2); 972, 961, 881 and 867. – NMR. (CCl_4): 1.15–2.80 (*m*, 8H); 4.70–5.15 (*m*, 1H, H—C(7), missing in 7-deuteriated **10b**); 5.50–5.70 (*m*, 2H, vinyl H); 7.67 (*d*, 4H, arom. H).

$C_{14}H_{15}BrO_3S$ (343.26) Calc. C 48.98 H 4.40% Found C 49.18 H 4.41%

exo-*Bicyclo[3.2.1]oct-2-en-7-yl acetate* (**11c**) *and* 7-[^2H]-**11c** (**11c**-7-d). 1.30 g (3.81 mmol) **10b** and 4 g (13.3 mmol) tetra(*n*-butyl)ammonium acetate [20] (from benzene m.p. 114–116°) were heated under reflux in 13 ml dry benzene for 23 h. Ether was added and the mixture washed with 2N aqueous Na_2CO_3-solution and water. After drying over K_2CO_3 the organic layer was evaporated (VRE.) and the residue glass-bulb distilled at 80°/11 Torr, yield 474 mg (75%) of oil which contained 90% *exo*-acetate **11c** according to GLC. on column B. – IR. (CCl_4): 3040 (vinyl-H); 1735 (C=O); 698 (*cis*-olefin); 2948, 1375, 1058, 1034, 1019, 988. – NMR. (CCl_4): 1.90 (*s*, 3H, CH_3COO); 4.8–5.0 (*m*, 1H, H—C(7), missing in **11c**-7-*d*); 5.2–6.0 (*m*, 2H, vinyl-H); 1.2–2.7 (*m*, 8H).

7-[^2H]-exo-*bicyclo[3.2.1]oct-2-en-7-ol* (**3**-*OH*-7-d). 564 mg (3.37 mmol) **11c**-7-*d* and 0.5 g (13.2 mmol) $LiAlH_4$ in 175 ml dry ether were stirred at 22° for 4 h 2 ml of aqueous 4% NaOH-solution were added and the mixture worked up as described for **10a**. Sublimation of the crude product at 80°/11 Torr yielded 344 mg (82%) crystals. These consisted of 90% *exo*-alcohol **3**-OH-7-*d* and 10% unidentified alcohol (probably the *endo*-isomer) as shown by GLC. The alcohol was converted to the 2,4-dinitrobenzoate as described [3]. From hexane/benzene m.p. 102–103° (lit. [3] undeuteriated, m.p. 100–102°). – IR. (CCl_4): 3120 (arom. CH); 3045 (vinyl CH); 2229 (C—D); 1735 (C=O); 1537 and 1350 (NO_2); 698 (*cis*-olefin); 2958, 1607, 1315, 1293, 1242, 1135, 1115, 1060, 955. – NMR. (CCl_4): 1.5–2.7 (*m*, 8H); 5.42–5.68 (*m*, 1H, H—C(3)); 5.77–6.00 (*m*, 1H, H—C(2)); 7.95 (*d*, J = 9 Hz, 1H, arom. H); 8,46 (*q*, 1H, arom. H); 8.65 (*d*, J = 2 Hz, 1H, arom. H). Very weak signal at 5.25 showed only trace of H—C(7). There are 93 ± 1% deuterium at C(7) as calculated from three integrations.

2.2. *3,5-Di-*[^2H]-endo-*tricyclo[3.2.1.0^{3,6}]octan-4-ol* (endo-**2**-*OH-3,5*-d_2). 3,5-Dideuteriated *endo*-**2**-OH was prepared as described for *endo*-**2**-OH [3] *via* ketone **7** using CD_2N_2 instead of CH_2N_2.

1.74 g (12 mmol) of the acid chloride **8b** from cyclopenten-3-yl acetic acid (**8a**) in 19 ml dry ether were treated with 1.5 g CD_2N_2[15]) and the crude diazoketone **8c** obtained (1.8 g) irradiated in 156 ml pentane. The resulting *3,5-Di-*[^2H]-*tricyclo[3.2.1.0^{3,6}]octan-4-one* (**7**) (1.6 g) was reduced with 660 mg (17.4 mmol) $LiAlH_4$ in ether to give 900 mg of semi-crystalline material after subli-

[15]) Prepared by the procedure of *Aldrich Chemical Co.* from N-methyl-N-nitroso-*p*-toluenesulfonamide and NaOD. The ethereal solution should not be dried over KOH so as to avoid D-exchange.

mation at 80°/11 Torr. GLC. showed this material to consist of 86% *endo*-**2**-OH, beside the *exo*-isomer and side products, which were separated by chromatography on silica gel as described [3].

The ^{1}H-NMR. spectrum of *endo*-**2**-OH-3,5-d_2 in the presence of 0.2 equiv. Eu(fod)$_3$ [3] differed from that of an undeuteriated sample. Thus, the integral for the C(3) and C(5) protons corresponded to *ca.* 1 proton and the C(4) proton signal was a dublett ($J = 6$ Hz) instead of a triplett. The average of several integrations indicated a total deuterium content of 88 ± 2%.

817 mg (6.58 mmol) *endo*-**2**-OH-3,5-d_2 yielded 1.45 g (70%) of the *2,4-dinitrobenzoate* [3]; after two crystallizations from *n*-hexane, m.p. 86–88° (Lit. [3]: 88.5–90°, undeuteriated).

2.3. *3-[^{2}H]-Tricyclo[3.2.1.0^{2,7}]octan-3-ol* (**1**-OH-3-*d*) was obtained by reduction of the ketone **6** with $LiAlD_4$ as described for the undeuteriated ketone [21]. The crude alcohol was purified by chromatography on silica gel. Elution with pentane/ether 3:2 and sublimation at 70°/11 Torr yielded pure **3**-OH-3-*d* in 90% yield, m.p. 137.5–139° (Lit. [3]: m.p. of undeuteriated material 138–140°). – IR. (CCl_4): 2160 (C–D) corresponding to C–H bonds at 2940 in **1**-OH. – ^{1}H-NMR. (CCl_4): the signal for the C(3) proton in **1**-OH at 4.17 ppm was absent.

The p-*nitrobenzoate* of **1**-OH-3-*d* was prepared as described [3] and recrystallized from pentane, m.p. 76.5–78° (Lit. [21] m.p. 77.5–80°). – The ^{1}H-NMR. spectrum (CCl_4) showed no signal at 5.45 ppm for the C(3) proton.

2.4. *4-[^{2}H]-endo-Tricyclo[3.2.1.0^{3,6}]octan-4-ol.* Reduction of 732 mg (6.00 mmol) of pure ketone **7** with 500 mg (12.00 mmol) $LiAlD_4$ in ether as described [3] furnished 718 mg (97%) of mixture of 89% *endo*-**2**-OH-4-*d* and 11% *exo*-isomer. Separation on a silica gel column with hexane/ether 3:2 yielded 600 mg (82%) *endo*-alcohol, m.p. 162–165°, and 60 mg (8%) *exo*-alcohol. – The ^{1}H-NMR. signal at 4.09 for the C(4) proton was absent in *endo*-**2**-OH-4-*d*.

The *2,4-dinitrobenzoate* was prepared as described [3] and recrystallized from *n*-hexane, m.p. 88.5–90° (Lit. [3] m.p. 88.5–90°). The IR. spectrum showed a C–D band at 2200. In the ^{1}H-NMR. spectrum the signal for the C(4) proton at 5.05 ppm was absent.

3. Preparation of methane sulfonates *18a* and *18b*. – 3.1. endo-*Tricyclo[3.2.1.0^{3,6}]oct-4-yl methanesulfonate* (**18a**). The usual methods for preparing alkyl and arylsulfonates employing a sulfonyl chloride and a base, such as pyridine or 1,4-diazabicyclo[2.2.2]octane (Dabco), failed due to the instability of **18a**. However, the method of *Truce* [22a] and *King & Durst* [22b] gave good results. 124 mg (1 mmol) of pure *endo*-**2**-OH were dissolved in 1 ml of dry benzene containing 111 mg (1.1 mmol) of triethylamine (distilled from CaH_2). After cooling to 5° 114 mg (1 mmol) of methanesulfonyl chloride in 2 ml of dry benzene were added with stirring. After 2 h at 7° triethylamine hydrochloride was filtered off and the solution was evaporated in a VRE. at 20°. **18a** is a colorless oil which is stable at −80° but rapidly decomposes to a colored product at room temperature. – IR. (CCl_4): 1370, 1345, 1200, 1180 (SO_2); 960 (S–O–R). – NMR. (measured at −40° in CCl_4): 1.57 (*s*, 2H, H–C(7)); 1.9–2.35 (*m*, 4H, H–C(2) and H–C(8)); 2.35–3.0 (*m*, 4H, H–C(1), H–C(3), H–C(5) and H–C(6)); 3.27 (*s*, 3H, CH_3SO_2); 5.25 (*t*, 1H, H–C(4)).

3.2. exo-*Tricyclo[3.2.1.0^{3,6}]oct-4-yl methanesulfonate* (**18b**) was prepared from *exo*-**2**-OH in the same way as **18a**. After sublimation at 80°/0.005 Torr crystals of m.p. 39–40°. – IR. (CCl_4): 1375, 1350, 1180 (SO_2); 955 (S–O–R). – NMR. (CCl_4): 1.38 (*s*, 2H, H–C(7)); 1.67 (br.*s*, 4H, C(2) und C(8)); 2.48 (*m*, 3H, H–C(1), H–C(3) and H–C(5)); 2.90 (*s*, 3H, CH_3SO_2); 3.2 (*t*, 1H, H–C(6)); 4.29 (*s*, 1H, H–C(4).

$C_9H_{14}O_3S$ (202.27) Calc. C 53.46 H 6.98% Found C 53.28 H 7.07%

3.3. exo-*Tricyclo[3.2.1.0^{3,6}]oct-4-yl* p-*toluenesulfonate* was prepared from *exo*-**2**-OH and *p*-toluenesulfonyl chloride in pyridine (24 h at −10°), m.p. 84–87.5°. – IR. (CCl_4): 1380, 1190, 1180 (SO_2); 960 (S–O–C).

4. Solvolyses of optically active esters. – 4.1. *Solvolysis of optically active* **1**-*O-Pnb*. Following the procedure described in [4] 233 mg (0.854 mmol) **1**-O-*Pnb* ($[\alpha]_D^{25} = -71.2°$, m.p. 79.5–81.5°) were dissolved in 43 ml 70% aqueous dioxane, containing 127.1 mg (1.27 mmol) of triethylamine. After heating to 60° for 7 h the cooled solution was diluted with 43 ml water and extracted three times with each 75 ml portions of pentane or ether. The extracts were washed with small amounts of water, dried over Na_2SO_4 and carefully concentrated by distilling off the solvent through a *Vigreux* column. The crystalline product was sublimed at 80°/11 Torr to yield 62.5 mg of a mixture of 83.5% alcohol **1**-OH and 16.5 mg **3**-OH, as determined by GLC. on column A. The specific optical rotation of the mixture in $CHCl_3$ was 0 ± 0.1°. The sublimation

residue (*ca.* 30 mg) consisted of rearranged *p*-nitrobenzoate, *i.e.* **3**-O-*Pnb*, which was also optically inactive.

4.2. *Solvolysis of optically active* **3**-*O*Dnb. 160 mg (0.50 mmol) **3**-O-*Dnb* ($[\alpha]^{25} = 31.4°$, m.p. 99–100°) were reacted in 90 ml 70% dioxane, containing 76 mg (0.75 mmol) of triethylamine, for 75 h at 80° and worked up as described under 4.1. The crude product was sublimed at 80°/11 Torr to yield a mixture of inactive **1**-OH and **3**-OH in a ratio of 4:1 (GLC. column A). The sublimation residue contained 15.8 mg of unreacted and partly racemized starting material, $[\alpha]_D = +10.5°$ ($c = 0.8$, $CHCl_3$).

4.3. *Optical stability of* **1**-*OH*. 20.4 mg (0.165 mmol) **1**-OH ($[\alpha]_D = -25.2°$), 35 mg (0.165 mmol) 2,4-dinitrobenzoic acid and 25.3 mg (0.25 mmol) triethylamine in 8.3 ml of 70% dioxane were kept at 60° for 4 h without loss of optical activity. After 61 h at 90° $[\alpha]_D$ had decreased to $-16.7°$.

5. Solvolyses of deuteriated esters in 70% dioxane. – 5.1. *Solvolysis of* **1**-*O*-*Pnb*-*3*-d. 548.6 mg (2.0 mmol) **1**-O*Pnb*-3-*d* in 70 ml 70% dioxane, containing 1.5 equiv. triethylamine, were warmed to 60° for 7 h. The reaction mixture was worked up as described under 4.1. to yield a mixture of 194.3 mg (78%) of **1**-OH and **3**-OH in the ratio 86:14 which was separated by chromatography on silica gel. The non-sublimable residue contained rearranged **3**-O*Pnb* (20%). The 100 MHz ^{1}H-NMR. spectra of the three products and those of authentic samples of **1**-OH, **3**-OH and **3**-O*Pnb* [3] were identical except for the absence of the signals for the C(3) protons at 4.17, 5.38 and 5.53, respectively (Table 1).

5.2. *Solvolysis of* endo-**2**-*O*Dnb-*4*-d. 450 mg (1.41 mmol) in 60 ml 70% dioxane containing 1.5 equiv. triethylamine were heated to 90° for 70 h. Work-up yielded 136 mg of a mixture containing 78% **1**-OH-2-*d*, 18% **3**-OH-2-*d* and 4% *endo*-**2**-OH-4-*d* (by hydrolysis). In addition 23 mg (5%) of non-sublimable, rearranged **3**-O*Dnb*-2-*d* were isolated [3]. From pentane m.p. 100–102°. – ^{1}H-NMR. (CCl_4): 8.60 (*d*×*d*, 2H) and 8.00 (*d*, 1H, aryl-H); 5.53 (*m*, 1H, H—C(3)); 5.20 (*d*×*t*, 1H, H—C(7)); 2.6 (br.*s*, 2H); 2.32 (br.*s*, 1H); 2.2-1.5 (*m*, 5H). No signal at 5.88 for H—C(2) (Table 1).

5.3. endo-**2**-*O*Dnb-*3,5*-d_2. 230 mg (0.72 mmol) and 109 mg (1.08 mmol) triethylamine in 34 ml 70% dioxane were heated to 80° for 25 h. Work-up yielded 80% **1**-OH and 20% **3**-OH which were purified by chromatography on 15 g silica gel. – ^{1}H-NMR. spectroscopy (100 MHz) in the presence of Eu(fod)$_3$ showed the deuterium distribution listed in Table 1.

5.4. *Solvolysis of* **3**-*O*Dnb-7-d. 231.5 mg (0,73 mmol) and 112.8 mg (1.12 mmol) triethylamine in 34 ml 70% dioxane were heated to 80° for 96 h. Work-up yielded 103.5 mg of a mixture of 78% **1**-OH and 22% **3**-OH. After sublimation at 80°/11 Torr and chromatography on 15 g silica gel the alcohols were analysed by 100-MHz-^{1}H-NMR. spectroscopy with addition of Eu(fod)$_3$ (Table 1).

5.5. *Solvolysis of* endo-**2**-*OH*-*3,5*-d_2 *with 1* N H_2SO_4. 52 mg (0.41 mmol) alcohol were dissolved in 7 ml dioxane, 2 ml water and 0.26 ml conc. sulfuric acid and warmed to 43° for 12 h. After dilution with 10 ml water the reaction mixture was extracted with ether. The ether extracts were washed with 2N Na_2CO_3 and water, dried over Na_2SO_4 and evaporated. The residue (55 mg) was sublimed at 60°/16 Torr to yield 44 mg (85%) of pure **3**-OH. – ^{1}H-NMR. analysis in CCl_4 with Eu(fod)$_3$ showed the following deuterium distribution: 28 ± 4% at C(1); 26 ± 7% at C(7); 46 ± 4% at C(3).

6. Solvolyses in formic acid. – *General procedure.* 2×10^{-2}M solutions of deuteriated esters (*ca.* 0.5 mmol) in dry formic acid were reacted under the conditions indicated below. The solutions were then diluted with an equal volume water and extracted several times with pentane. The extracts were washed with 2N Na_2CO_3 and with water, dried over Na_2SO_4 and evaporated in a VRE. The residue was glass-bulb distilled at 76°/12 Torr and the resulting pure formate of **3**-OH (checked by GLC. on column B) analysed with a 13.81- MHz-*Bruker* HX-90 ^{2}H-NMR. *Fourier* transform spectrometer[16]) in CCl_4, using C_6F_6 as external standard, with 900–3200 scans (Table 1).

a) **1**-*O*Dnb-*3*-d was reacted at 50° for 24 h and yielded 95% of oily **3**-OCHO;

b) endo-**2**-*O*Dnb-*3,5*-d_2 was reacted at 50° for 24 h and yielded 50% of oily **3**-OCHO;

c) **3**-*O*Dnb-7-d was reacted at 50° for 40 h to yield 80% **3**-OCHO.

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d) endo-**2**-*O*Dnb-*4*-d yielded 94% **3**-OCHO. Since no deuterium scrambling occurred deuterium analysis was carried out by ^{1}H-NMR. spectroscopy which revealed no signal for a proton to C(2) at 5.87 ppm.

7. Solvolyses of *exo*-tricyclo[3.2.1.0^{3,6}]octan-4-ol derivatives in 70% dioxane containing 1.5 equiv. of triethylamine, were carried out as described under 4.1. The products were analysed by GLC. (column B). Reaction of the p-*toluenesulfonate of* exo-**2**-*OH* at 90° for 7 h yielded 78.5% **1**-OH and 21.5% **3**-OH. The *methanesulfonate of* exo-**2**-*OH* at 80° for 15 h yielded 81% **1**-OH and 19% **3**-OH.

8. Kinetic measurements were carried out as described [4] with a *Konduktoskop Metrohm E* 365 combined with a recorder *Labograph E 478*. The solvent (70 vol.% dioxane) was prepared by mixing 700 ml (723.63 g) purified dioxane (d_4^{20} 1.03375) and 300 ml (299.47 g) water.

Polarimetric rate constants (k_α) of optically active **1**-O*Pnb* and **3**-O*Dnb* were measured in 70% dioxane, containing 1.5 equiv. of triethylamine, using the ampoule method [23]. *Rotations* were determined with a *Perkin-Elmer Polarimeter Model 141* and k_α calculated by the formula $2.303 \log (\alpha_0-\alpha_\infty)/(\alpha-\alpha_\infty) = k_\alpha t$. k_α for **1**-O*Pnb* at 60.06° was $6.22 \times 10^{-4} \pm 0.089$; for **3**-O*Dnb* at 90.00° $3.35 \times 10^{-5} \pm 0.029$.

Elemental analyses by Mr. *E. Thommen*.

REFERENCES

[1] Carbonium Ions Vol. III, edit. by *G. A. Olah & P. von R. Schleyer, Wiley-Interscience*, New York 1972; a) Chap. *23*, p. 1007; chap. *25*, p. 1201; chap. *26*, p. 1295.

[2] *G. A. Olah, C. L. Jeuell, D. P. Kelly & R. D. Porter*, J. Amer. chem. Soc. *94*, 146 (1972); *G. A. Olah & G. Liang*, ibid. *97*, 1920 (1975).

[3] *M. Geisel, C. A. Grob, W. Santi & W. Tschudi*, Helv. *56*, 1046 (1973).

[4] ibid., Helv. *56*, 1055 (1973).

[5] *R. B. Woodward & T. J. Katz*, Tetrahedron *5*, 70 (1959); *C. Djerassi & J. Staunton*, J. Amer. chem. Soc. *83*, 736 (1961).

[6] *M. Geisel, C. A. Grob, W. Santi & W. Tschudi*, Tetrahedron Letters *1972*, 4311.

[7] *K. B. Wiberg & B. A. Hess*, J. Amer. chem. Soc. *89*, 3015 (1967).

[8] a) *S. Winstein & R. Adams*, ibid. *70*, 838 (1948); b) *S. Winstein & E. M. Kosower*, ibid *81*, 4399 (1959); c) *J. D. Roberts & R. H. Mazur*, ibid. *73*, 2509 (1951).

[9] a) *K. B. Wiberg*, Tetrahedron *24*, 1083 (1968); b) *J. E. Baldwin & W. D. Foglesong*, J. Amer. chem. Soc. *90*, 4303 (1968).

[10] *M. Simonetta & S. Winstein*, ibid. *76*, 18 (1954).

[11] *M. Vogel & J. D. Roberts*, ibid. *88*, 2262 (1966).

[12] *R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver & J. D. Roberts*, ibid. *81*, 4390 (1959).

[13] *J. D. Roberts & R. H. Mazur*, ibid. *73*, 3542 (1951); *C. G. Bergstrom & S. Siegel*, ibid. *74*, 145 (1952).

[14] *P. von R. Schleyer & G. W. Van Dine*, ibid. *88*, 2321 (1966); *J. A. Berson, G. M. Clarke, D. Wege & R. G. Bergman*, ibid. *90*, 3238 (1968); *W. J. Hehre & P. C. Hiberty*, ibid. *94*, 5917 (1972); *Y. E. Rhodes & V. G. DiFate*, ibid. *94*, 7582 (1972); *S. J. Cristol & D. A. Beimborn*, ibid. *95*, 3651 (1973).

[15] *R. E. Leone & P. von R. Schleyer*, Angew. Chem. *82*, 889 (1970); internat. edit. *9*, 860 (1970).

[16] *Z. Majerski, S. Borcic & D. E. Sunko*, Tetrahedron *25*, 301 (1969); Chem. Commun. *1970*, 1636.

[17] *Z. Majerski & P. von R. Schleyer*, J. Amer. chem. Soc. *93*, 665 (1971).

[18] *K. B. Wiberg & G. Szeimies*, ibid. *92*, 591 (1970).

[19] *M. Fétizon & M. Golfier*, Tetrahedron Letters *1972*, 4445.

[20] *W. E. Thompson & C. A. Kraus*, J. Amer. chem. Soc. *69*, 1016 (1947).

[21] *R. R. Sauers, J. A. Beisler & H. Freilich*, J. org. Chemistry *32*, 569 (1967).

[22] *W. Truce, R. Campbell & J. Norell*, J. Amer. chem. Soc. *86*, 288 (1964); *J. F. King & J. Durst*, ibid. *86*, 287 (1964).

[23] *C. A. Grob & S. Winstein*, Helv. *35*, 782 (1952).