59. Nature of the 5-norbornen-2-yl Cation Intermediate in the Acetolysis of 2-deuterio-*endo*-5-norbornen-2-yl Brosylate

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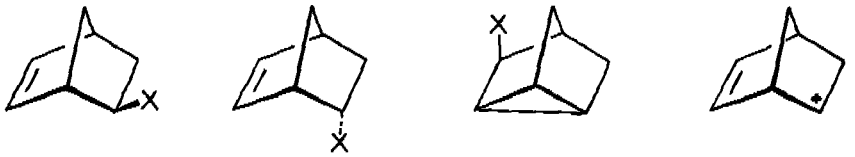
Summary. Mass spectrometrical and ^{1}H-NMR.-analyses of the *exo*-5-norbornen-2-yl acetate, formed by acetolysis of *endo*-5-norbornen-2-yl-2-*exo*-d brosylate, demonstrate that the deuterium initially on C(2) migrates partially (30%) onto C(1) (mechanism Ia or Ib). No deuterium could be detected on the other positions, which shows that C(1–7) migration is insignificant. ^{13}C-NMR.-analysis of the deuteriated nortricyclyl acetate obtained as main product shows that the deuterium is equally and uniquely distributed between positions C(1) and C(6). This indicates that the nortricyclyl derivatives do not arise from nucleophilic attack on C(5) of asymmetrical norbornenyl intermediates, but from the reaction of a symmetrical nortricyclyl cation intermediate with solvent (mechanism Ib).

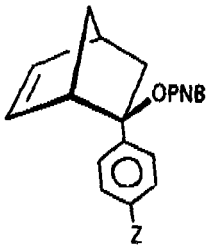
Since the pioneering work of *Roberts* [1] and *Winstein* [2] on the solvolysis of *exo*- and *endo*-5-norbornen-2-yl derivatives **1-X** and **2-X** many papers have dealt with the cationic intermediate, the nature of which has still not been established satisfactorily [3]. We discuss briefly the main features of this homoallylic system and present experimental results that allow, for the first time, a clear distinction between five possible mechanisms Ia, Ib, II, III and IV of the degenerate rearrangement of the cationic intermediate formed in the acetolysis of the *endo*-5-norbornen-2-yl brosylate.

Introduction. – The participation of the C(5–6) double bond in the solvolysis of *exo*-5-norbornen-2-yl derivatives **1**-X was indicated by the relative rate of acetolysis of *exo*-5-norbornen-2-yl *p*-bromobenzenesulfonate (**1**-OBs), which was found to be

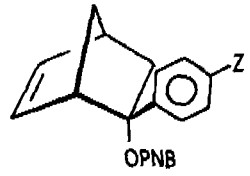


1–X **2–X** **3–X** **4**

7000 times as fast as the rate of the *endo*-5-norbornen-2-yl isomer (**2**-OBs) at 25° [2] [4], and by the formation of *exo*-5-norbornen-2-yl acetate and nortricyclyl acetate as major products. *Brown* [5] found no evidence for the above π-participation in the solvolyses of *exo*- and *endo* 2-aryl-5-norbornen-2-yl *p*-nitrobenzoates (**1Ar**-OPNB and **2Ar**-OPNB), and attributed the high *exo*:*endo* ratio of *ca.* 300 not to an enhanced *exo* rate, but rather to a retarded *endo* rate due to steric hindrance of ionization by the bulky π-cloud of the C(5–6) double bond. Although the experimental data presented thus far are impressive they do not exclude C(1–7) participation in the ionization of the *endo* compounds **2**-X. This participation could involve bridging as in **6** → **7**, or hyperconjugation as in **8** → **9** and might offer an alternative explanation



1Ar-OPNB



$Z = CH_3O$-, H-, CF_3-

2Ar-OPNB

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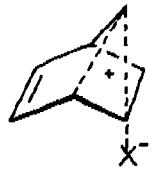


6

8

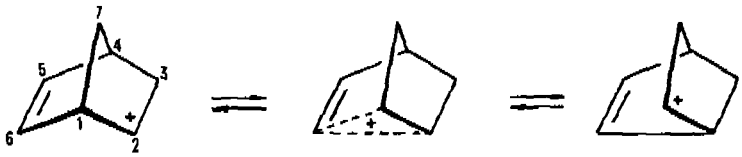
7

9

for the constant *exo*:*endo* rate ratios observed for 2-aryl-5-norbornen-2-yl systems (**1Ar**-OPNB and **2Ar**-OPNB) with varying electron demand at the C(2) centre[1]).

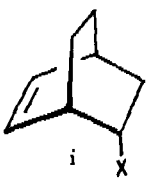
Kirmse showed that 1.2–1.3% of derivatives of the 3-norpinen-2-yl cation (**7**) besides **1**-X and **3**-X products are formed by irradiation of the tosylhydrazone of dehydronorcamphor in strong nucleophilic media [6]. Although the conditions of this experiment were rather different from those normally used in solvolysis of **1**-X and **2**-X derivatives, it indicates that the C(1–7) bond can migrate. The intervention

Mechanism Ia



4 **10** **4'**

[1]) It is of interest to mention the solvolysis of the homologous 5-bicyclo[2.2.2]octen-2-yl system, the *endo* derivatives (i) of which undergo migration of the σC(1–7) bond, while the *exo* derivatives (ii) yield products resulting from π-participation of the homoallyl cation system [3].



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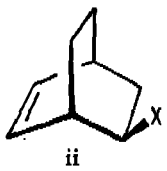
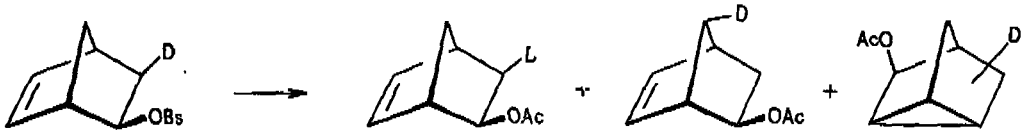


ii

of the norpinenyl cation **7** in the interconvertion of dehydronorbornyl cations cannot therefore be excluded *a priori*[2]).

In the acetolysis and formolysis of **1**- and **2**-OBs or deamination of **2**-NH_2, *Roberts* [12] observed that 30 to 48% of the initial ^{14}C label at C(2,3) had migrated into the other positions C(1,4,5,6,7) of the *exo*-5-norbornen-2-yl products. These results suggested the occurance of an equilibrium between two asymmetrical cationic intermediates **4** and **4'** *via* a symmetrical intermediate or transition state of type **10**, *i.e.* a *Wagner-Meerwein* rearrangement involving the migration of the C(1–6) bond. Depending upon the reaction conditions and particularly upon the reactivity of the nucleophile, the label scrambling was partial or complete. This interpretation is supported by the solvolysis of 2-deuterio-**1**-X derivatives [13] and by DCl additions to norbornadiene and quadricyclane [14].

In the acetolysis of *exo*-3-deuterio-**1**-OBs *Cristol* [15] observed that the deuterium is distributed equally between the *exo*-3 and *syn*-7 positions of the **1**-OAc isolated.



It was further shown that the deuterium migration in the starting brosylate was faster than nucleophilic attack by solvent yielding **1**-OAc and **3**-OAc. In contrast to *Robert*'s conclusion it was suggested that a symmetrical cation intermediate of type **10** is primarily formed, thus removing the necessity of an asymmetrical norbornenyl cation intermediate[3]). The participation and migration of the C(1–6) bond, as implied by *mechanism Ia*, is reasonable by analogy to the 'non-classical' norbornyl cation [17]. An alternative *mechanism Ib* involves the nortricyclyl cation **11** as an intermediate in the **4** $\rightleftarrows$ **4'** rearrangement. The latter represents a homoallyl-cyclopropylmethyl cation rearrangement [18] and is consistent with the formation of nortricyclyl products **3**-X and with the reported label experiments. If the rearrangement **4** $\rightleftarrows$ **11** takes place, it is of extreme interest to determine experimentally whether any stereoelectronic factors due to the rigid geometry of **11** raise an energy

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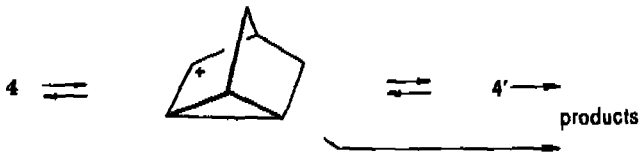
[2]) An estimation of the formation enthalpies of **4** and **7** indicates that the difference of strain energy between norpinene and norbornene (*ca.* 18 kcal/mol [7]) is compensated by the stabilization gained in conversion of a homoallyl to an allyl cation, *i.e.* **4** to **7**. This stabilization is estimated to be 11–18 kcal/mol from the activation energies of 18 and 16 kcal/mol measured for the hydrogen migration in the 2-cyclopenten-1-yl [8] and 2-cyclohexen-1-yl cations [9] respectively. These energy barriers are composed of the enthalpy difference between homoallyl and allyl cations and of the activation energy of the hydrogen migration that can be considered lower than 5 kcal/mol as observed in the cyclopentyl cation [10] and other aliphatic carbenium ions [11].

[3]) Depending upon the reaction conditions, it is obvious that species such as starting material, tight ion pairs, solvent separated ion pairs and separated ions may be responsible for a large variation in the solvolysis outcome [16]. Consequently a distinction between symmetrical and asymmetrical intermediates may become difficult. For instance, the symmetrical nortricyclyl cation **11** or the bridged cation **10** can react with solvent as asymmetrical ion pair intermediates.

Mechanism Ib



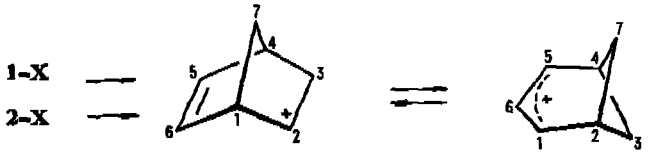
11

barrier independently of the solvent and the nucleophile[4]). The isolated nortricyclyl cation **11** is expected to be much more stable than the norbornenyl cation **4** since **3**-X derivatives are thermodynamically more stable than **1**-X and **2**-X derivatives [20] and because the secondary cation **11** benefits from the strong stabilization of the favorably oriented cyclopropane ring [18b] [21].

Mechanisms Ia and *Ib* interchange the C(1) and C(2), the C(3) and C(7) centres and as well as the *exo*-3 and *syn*-7 positions synchronously.

If C(1–7) participation is effective[5]) it may lead to the migration of that bond to form various possible cationic intermediates as indicated by the hypothetical *mechanisms II*, *III* and *IV*.

Mechanism II



4 **7**

Mechanism II involves an equilibrium of **4** with the norpinenyl cation **7** that interchanges the C(1) and C(5) and C(2) and C(4) centres synchronously and the C(3) and C(7) centres independently. The *exo*-3 and *syn*-7 interchange as in *mechanism Ia* and *Ib* if the migration of C(7) is viewed as a [1,2]sigmatropic shift that requires configuration retention at C(7) and C(3) respectively [25]. Theoretically [26], this isomerization could proceed through an intermediate **9** in a fashion similar to the lower homolog: *bicyclo[3.1.0]hex-3-en-2-yl cation* [27]. In this case the bisected form

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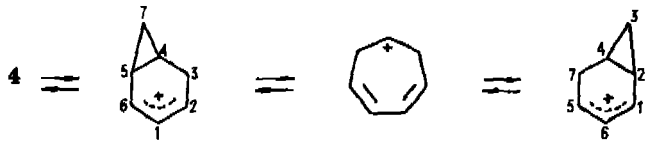
[4]) No stable minimum corresponding to the homoallyl cation CH_2=CH—CH_2—CH_2^+ was found on the $C_4H_7^+$ potential surface by *ab initio* MO calculations; all possible structures seemingly collapse without energy to the bisected form of the cyclopropylmethyl cation [19].

[5]) In norbornadiene the C(1–7) bond has been found to be 0,035 Å longer than C(1–2) bond [22]. This suggests that the C(1–7) bond in norbornenyl cation **4** should interact better with the positively charged C(2) centre than the C(1–6) bond. Furthermore, the orientation of the C(1–7) bond is as good as the C(1–6) bond orientation for a strong interaction with the forming p orbital. Some reserve should, however, be excercised in interpreting bond lengths in rigid bicyclic systems such as norbornane and norbornadiene where the value measured varies inside large limits from one author to the other [7a] [23]. Furthermore, internuclear repulsion [24] can be an imdortant factor in determining the energy and geometry of the norbornenyl system, and may render the C(1–6) bond longer than normal σ allylic bonds in open chain systems.

of **9**, leading to the interchange of *exo*-3 and *anti*-7 positions, is expected to be more stable than an eclipsed form of **9**.

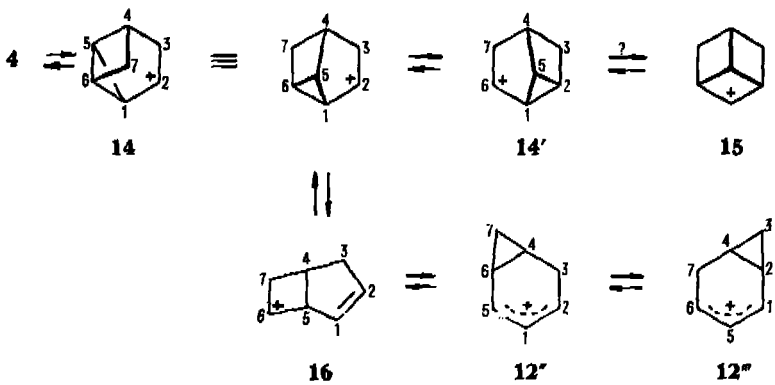
Mechanism III



12 **13** **12'**

A [1,3]sigmatropic shift [28] of the C(1–7) bond of the homoallyl cation **4** could lead to the bicyclo[4.1.0]hept-3-en-2-yl cation **12**[6]). The equilibrium **12** ⇄ **12'**, which possibly involves the cation **13** scrambles C(1) and C(6), C(2) and C(5) and C(3) and C(7) synchronously, C(4) staying unchanged. The cation **12** could arise by a [1,4]-sigmatropic shift from **7**. This process (**4** ⇄ **7** ⇄ **12** ⇄ **12'**) would scramble the carbons as indicated for *mechanisms II* and *III*. The cation **12** could also be obtained by a cyclobutyl-cyclopropylmethyl rearrangement of the bicyclo[3.2.0]hept-2-en-7-yl cation **16**[7]) (see *mechanism IV*), that is formed by isomerization of the 3-*ψ*-nortricyclyl cation **14**. In contrast to mechanism III, the process **4** ⇄ **14** ⇄ **16** ⇄ **12''** ⇄ **12'''** scrambles the carbons C(1) and C(5), C(2) and C(6) and C(3) and C(7)[7]).

Mechanism IV



14 **14'** **15**

16 **12''** **12'''**

Mechanism IV describes the migration of the C(7) bridge from C(1) to C(6), which leads to the formation of the 3-*ψ*-nortricyclyl cation **14**. In the hydrolysis of *exo*- and *endo*-3-*ψ*-nortricyclyl paranitrobenzoate (**14**-OPNB), nortricyclanol (**3**-OH) was formed [30], therefore rendering reasonable the intervention of a cation such as **14** as an intermediate in the norbornenyl-nortricyclyl rearrangement. The cation **14**

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[6]) The allylic cation **12** is estimated to be at least 5 kcal/mol more stable than the homoallylic cation **4**.

[7]) *Kirmse et al.* [29] found that the cation **16**, generated in strong nucleophilic media, leads to the formation of products that are derivatives of cations **12**, **13**, and **14**, thus rendering our hypothesis reasonable. We thank Professor *W. Kirmse* for informing us about these results prior to publication.

may undergo a degenerate cyclopropylmethyl-cyclopropylmethyl rearrangement leading to the synchronous interchange of the C(2) and C(6) and the C(3) and C(7) centres.

To our knowledge no experiment has been reported that allows a distinction to be made between the five mechanisms outlined above. The degradation method used by *Roberts* [12] did not distinguish between C(1,4,5,6,7) in the norbornenyl products. ^{1}H-NMR.-spectroscopy allowed the observation of the *exo*-3 $\rightleftarrows$ *syn*-7 migration of deuterium; the mass spectrometrical determination of the deuterium content in the retro-*Diels-Alder* fragments of the deuteriated **1**-OAc obtained by acetolysis of 2-deuterio- [13] or 3-deuterio-5-norbornen-2-yl brosylates [15] only measures the amount of label that was transfered from C(2,3) to the C(1,4,5,6,7) positions without distinguishing between them. Therefore our first goal was the realization of an experiment that allows the distinction between *mechanisms I* (*a*, *b*), *II*, *III* and *IV*. It was anticipated that the solvolysis of *endo*-5-norbornen-2-yl brosylate (**2**-OBs) in buffered, boiling acetic acid would constitute the best system to test the occurance of C(1–7) migration as in *mechanisms II*, *III* and *IV*. A deuterium label on C(2) is expected to migrate onto C(1), C(4), C(5) or C(6) if *mechanisms I* (*a*, *b*), *II*, *III* or *IV* respectively are operative.

Results and discussion. – Dehydronorcamphor was reduced with $NaBD_4$ and yielded a 15:85 mixture of *exo*:*endo* 5-norbornen-2-ol-2-d (> 97% D) and then converted to a mixture of brosylates. Selective hydrolysis in aqueous acetone removed the *exo* isomer. Acetolysis of the resulting 2-deuterio-**2**-OBs was carried out in conditions similar to those used by *Roberts* [12] for **2**-^{14}C-2,3-OBs and yielded a 18 $\pm$ 2: 82 $\pm$ 2 of deuteriated **1**-OAc and **3**-OAc that were separated by preparative GLC. and analyzed by mass spectrometry and ^{1}H- and ^{13}C-NMR. techniques.

The deuterium content in **1**-OAc was measured by mass spectrometry and found to be 97 $\pm$ 1% D. Analysis of the cyclopentadiene fragment ($m/e^+ = 66$ amu) showed that 29 $\pm$ 1% of the deuterium label was distributed among the C(1,4,5,6,7) centres, corresponding to a total of 30 $\pm$ 1% of hydrogen scrambling. This result is in complete agreement with the 30.1% of carbon scrambling reported by *Roberts* [12]. It can therefore be concluded that less than 2% 3 $\rightarrow$ 5,6 hydrogen migrations or proton elimination and addition[8]) occur. Furthermore, the results show that deuterium labelling can be used in our case to follow the carbon migrations. The ^{1}H-NMR.-spectrum of **1**-d-OAc shows that 30 $\pm$ 4% of the original deuterium in C(2) has migrated mainly into the indistinguishable C(1) and C(4) positions. The deuterium content on C(5,6,7) is observed to be less than 5%. Therefore, if *mechanisms III* and/or *IV* are operative, they affect the overall reaction by less than 10%. If C(3) $\rightarrow$ C(2) hydrogen migration had occured in the solvolysis, the ^{1}H-NMR.-spectrum should show a deuterium loss on C(2) by more than 30% (the value measured by mass spectrometry and ^{14}C scrambling experiments) and some deuterium should be detectable on C(3) and C(7). Therefore one can conclude that C(3) $\rightarrow$ C(2) hydrogen

[8]) In basic media, such as KOH/DMSO/'crown ether', we found that **2**-OH eliminates water and yields norbornadiene as main product. In AcOH norbornadiene is known to add one mole of AcOH and form **1**-OAc and **3**-OAc [15]. Preliminary results indicate that solvolysis of **1**-OBs and **2**-OBs in non-buffered CF_3COOH do not yield the usual mixture of **1**-X and **3**-X [31].

migration contributes less than 4–5% to the deuterium scrambling in the **1**-d-OAc. Close examination of the olefinic ^{1}H-NMR. pattern (see Fig. 1) of **1**-d-OAc indicates that the deuterium that has migrated is located on only one of the bridgehead positions C(1) or C(4) since only one of the C(6) or C(5) hydrogens is affected by the deuterium coupling[9]). Addition of a lanthanide induced shift reagent [33] such as tris(dipivalomethanato)europium ($Eu(dpm)_3$) allows the separation of H(1) and H(4) signals, and the assignment of the H(1,4,5,6) signals (see Fig. 1 and 2). Integration of the separated ^{1}H-NMR. signal of H(1) and H(4) shows that at least 95% of

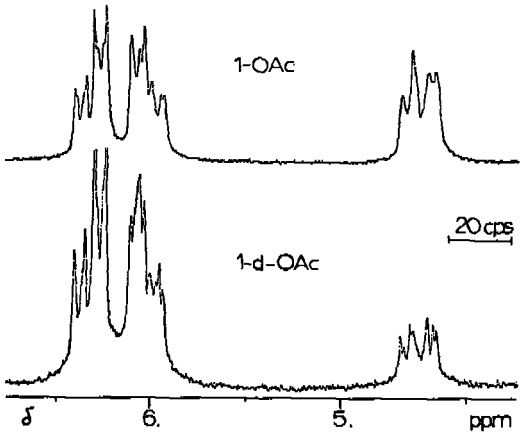

Fig. 1. *^{1}H-NMR.-spectra of* **1**-*OAc and* **1**-*d-OAc in $CDCl_3$ (Bruker* WP60, FT mode; $\delta_{TMS} = 0$ ppm)

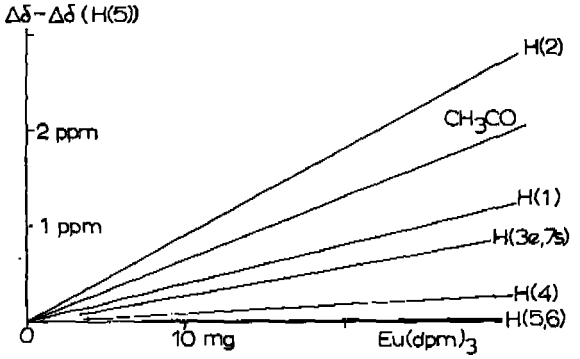

Fig. 2. *$Eu(dpm)_3$ induced shifts on the ^{1}H-NMR.-signals of* **1**-*d-OAc*
(34 mg in approx. 0.5 ml of $CDCl_3$; 40°)

the deuterium that has migrated was transfered from C(2) to C(1). These results indicate that *mechanisms Ia* or *Ib* account for more than 90% of the products formed in the buffered acetolysis of *endo*-5-norbornen-2-yl brosylate. There is no evidence for C(1–7) participation, although it cannot be excluded.

The ^{13}C-NMR.-spectrum of the deuteriated nortricyclyl acetate **3**-d-OAc shows that the deuterium is equally and uniquely distributed between C(1) and C(6) that correspond to the C(1) and C(2) positions in the norbornenyl system (see experi-

[9]) $J_{H(1,5)} \approx J_{H(4,6)} = 1$ to 0 Hz [32]; 4–5% of deuterium on C(1) or C(4) lead to a detectable modification of the olefinic ^{1}H-NMR. pattern.

mental part). This observation indicates that nortricyclyl products do not arise from an homoallyl S_N2' type reaction of the nucleophile on the C(5) carbon of the starting material **2**-OBs or an equivalent ion pair intermediate. Our findings show that a symmetrical intermediate of type **11** is responsible for the formation of nortricyclyl acetate. One cannot as yet tell whether the 1-deuterio-**1**-OAc is formed by quenching of a cationic intermediate **4'**, (arising from C(1,6) migration or by isomerization of **11**) or by nucleophilic attack on C(1) of the nortricyclyl cation intermediate **11**. It appears, however, that a part, if not all, of the 2-deuterio-**1**-OAc arises from reaction of the asymmetrical norbornenyl cation **4** with solvent[10]).

Conclusion. Buffered acetolysis of *endo*-5-norbornen-2-yl brosylate did not yield products resulting from a C(1–7) migration or from fragmentation. If *mechanisms II, III* or *IV* are involved at all, their contribution to the rearrangement of the 5-norbornen-2-yl cation **4** is less than 10% (limit of NMR. detection). The incomplete scrambling of deuterium between the C(1) and C(2) positions of the norbornenyl acetate could be explained by *mechanism Ia* involving the *Wagner-Meerwein* migration of C(1–6) bond. However, the scrambled norbornenyl products could also arise by way of a symmetrical nortricyclyl cation or ion pair as implied by *mechanism Ib*. The latter accounts for the formation of nortricyclyl acetate where the deuterium is found equally and uniquely distributed between C(1) and C(6) positions that correspond to C(1) and C(2) positions in the norbornenyl system. In buffered acetic acid the isomerization of norbornenyl cation **4** into nortricyclyl cation **11** is competitive with the reaction of these intermediates with solvent.

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Experimental Part.

*Preparation of the 2-deuterio-*endo*-5-norbornen-2-yl brosylate* (2-d-**2**-OBs). 3.1 g (28.7 mmol) of dehydronorcamphor in 60 ml of anhydrous THF were heated under reflux in presence of 1.15 g (27.5 mmol) of $NaBD_4$ 98% D (*E. Merk* AG, Darmstadt) for 24 h. After addition of 10 ml of H_2O, then 5 ml of 1N H_2SO_4, the alcohol mixture was extracted several times by ether. The ethereal extract was washed by sat. aq. $NaHCO_3$ and then with H_2O. Solvent removal left a white cristalline product that was dried under vacuum over solid paraffin. Yield: 2.6 g (82%) of a 85:15 (by ^{1}H-NMR.) mixture of *endo*:exo 2-d-norbornenols 97 ± 1% D (by mass spectrometry). The corresponding brosylate mixture was obtained using known procedures [13] [15]. The *exo* derivative was eliminated by selective hydrolysis (acetone/water 75:25; 30 min. at 45°). Pure, white cristalline 2-deuterio-**2**-OBs was isolated after recristallization in petroleum ether. Yield: 62%; m.p.: 84° (uncorrected) [2]. – IR (KBr): 3050; 2980; 2860; 2400; 1580; 1470; 1360; 1180; 1020; 950 cm^{-1}.

*Acetolysis of 2-d-***2***-OBs.* 0.5M solutions of 2-d-**2**-OBs in pure AcOH containing 2% of acetic anhydride and 0,52 mol anh. AcOK were heated under reflux and N_2 (bath temp.: 125 ± 5°) for 48 h. After elimination of AcOH by distillation and extraction with diluted aq. NaOH, the 18 ± 2: 82 ± 2 mixture of norbornenyl and nortricyclyl acetates was isolated by distillation under reduced pressure. Yield: 77%, colourless liquid. Preparative GLC. (*Aerograph, Wilkens Instruments and Research*, No. 31.012; column: Carbowax 20 M 15% on Chromosorb WAW 60/80 mesh, l = 2 m., int. diam. = 8 mm, T = 100 → 150°, H_2 flow: 60 ml/min.) allows the separation and purification of **1**-d-OAc and **3**-d-OAc.

[10]) **1**-OBs yielded incompletely label-equilibrated norbornenyl products [12] [13] in agreement with this hypothesis.

Product analysis. At least 10 mass spectra were recorded at various source pressures (70 eV) for the determination of the deuterium content in the deuterated-**1**-OAc fragments (*Bell & Howel* Mod. 21–490). – ^{1}H-NMR.- spectra were recorded with a *Varian* A60A and a *Bruker* WP60 spectrometer. Internal TMS in $CDCl_3$ was used as reference. Integration measurements were performed electronically and by 'xeroxing-cutting-weighing technique'. The CH_3-signal of the acetate was used as integration reference. The effect of $Eu(dpm)_3$ on the chemical shifts of **1**-OAc was strongly dependent upon the concentration of the acetate and the solvent ($CDCl_3$ – CCl_4). Nevertheless, the lanthanide induced shift on each ^{1}H-NMR. signal stays linear with the concentration of added $Eu(dpm)_3$ in a first approximation (see fig. 2).

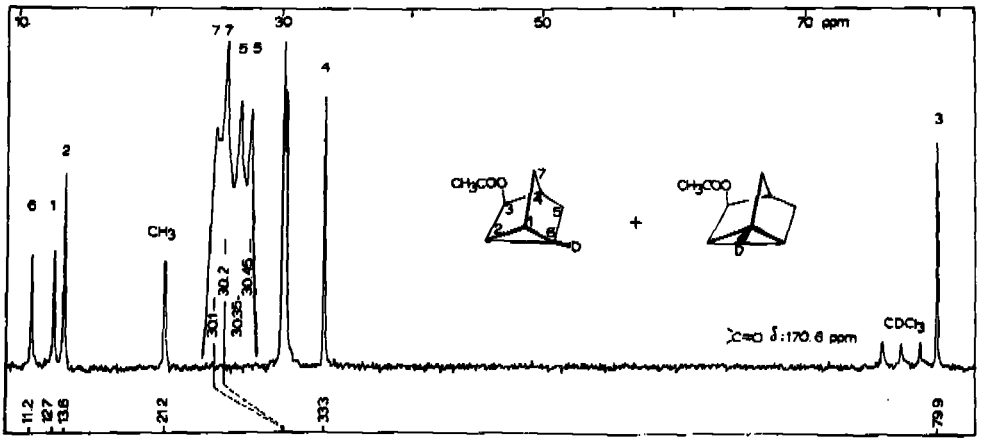

Fig. 3. *^{13}C-NMR. spectrum of* **3***-d-OAc in* $CDCl_3$

^{13}C-NMR.-spectra were recorded with a *Bruker* HX90 instrument (FT mode) using $CDCl_3$ as solvent and deuterium lock. The signals of the ^{13}C bearing a deuterium and no hydrogen were 'removed' from the spectrum by saturation (see fig. 3). Measurement conditions were set to render visible only the carbons bearing at least one hydrogen (^{1}H) that relaxed. Figure 3 shows that triplets due to the ^{13}C-D (distinguishable from the ^{13}C-H singlets) become unnoticeable in such conditions. Moreover, since there are 6–7 mol of $CDCl_3$ for 1 mol of **3**-d-OAc, the residual triplet of $CDCl_3$ allows an estimation of a maximum contribution of 2–5% for the ^{13}C-D signals to the observed ^{13}C-H signals. Integration of the ^{13}C-H signals was done by the 'xeroxing-cutting-weighing technique'; measurements of the peak heights yielded similar values although they might be affected by line broadening resulting from different β, γ, δ-deuterium shift on the observed ^{13}C-H signals of **3**-d-OAc [34]. By comparing the spectra of **3**-OAc and **3**-d-OAc recorded in the same conditions, the ^{13}C(1,6) signals show that 48 $\pm$ 4% and 50 $\pm$ 4% of the deuterium is present on C(1) and C(6) respectively. This observation implies that all the original deuterium substitutes C(1,6) by more than 90%. This result is confirmed by the splitting (see fig. 3) observed in the two $^{13}CH_2$(5,7) signals that is due to β-γ-deuterium shift on those carbons by the deuterated C(6,1) centres. The absence of further splitting or noticeable line broadening of the ^{13}C(2,3,4) signals also indicates that the deuterium substitutes C(1,6) only. Our signal assignment is consistent with those from ^{13}C-NMR. spectra of other nortricyclyl derivatives [35]; nevertheless, we do not claim that the distinction between C(5)/C(7) and C(1)/C(6) is definitive.

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