107. The Homoallyl-Cyclopropylcarbinyl Cation Rearrangement in the Solvolyses of *exo*- and *endo*-5-Norbornen-2-yl *p*-Bromobenzenesulfonates. Application of ^{2}H-NMR. Spectroscopy[1])

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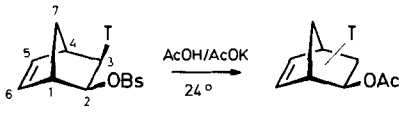
Summary

The buffered trifluoroethanolyses and acetolyses of *exo*-(2-D)- (**6**) and *endo*-(2-D)-5-norbornen-2-yl brosylates (**7**) yielded *exo*-5-norbornen-2-yl and 3-nortricyclyl derivatives. The deuterium distribution in these products was determined unambiguously by ^{2}H-NMR. and MS. In contrast to previous reports, each hydrogen and, consequently, each deuterium atom could be identified. Product ratio and label distribution in the solvolysis of **6** make unnecessary the intervention of asymmetrical homoallylic cation intermediates. The results are most economically rationalized by invoking symmetrical 3-nortricyclyl ion-pair intermediates.

Introduction. – Since the pioneering work of *Roberts* [2] and *Winstein* [3] on the solvolyses of *exo*- and *endo*-5-norbornen-2-yl derivatives, several authors have attempted to establish the nature of the carbocations involved [4–11]. *Lee* [7] reported the following tritium distribution in the *exo*-5-norbornen-2-yl acetate obtained by buffered acetolysis of (*exo*-3-T)-*exo*-5-norbornen-2-yl brosylate:



T at C(2): 12.4%, C(3): 36% } 48.4%

C(1,4,7): 40.1%, C(5,6): 11.5% } 51.6%

These results appeared to provide a rationalization of the discrepancies reported by *Roberts* [4] and *Lee* [10] and by *Cristol* [5], *Kirmse* [8] and *Goering* [9]. It was suggested that the solvolysis involves a pair of enantiomeric homoallyl cations **1** and **2** equilibrating *via Wagner-Meerwein* and 3,2-hydride shifts. These inter-

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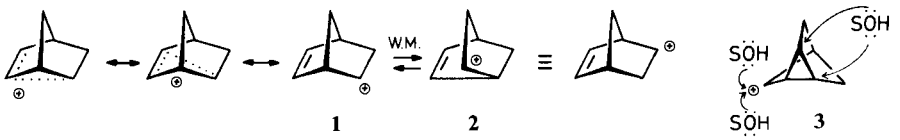

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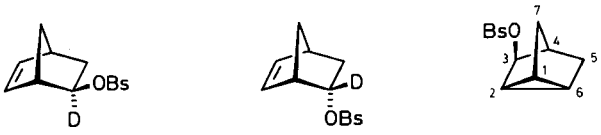
mediates can further eliminate a proton to form norbornadiene before capture by the solvent [7]. Recent experimental evidence from studies of stable cationic species in solution [12] and in the gas phase [13], as well as 'improved' MO-calculations [14] suggest that the symmetrical cyclopropylcarbinyl cation **4** is not the unique energy minimum on the $C_4H_7^+$ hypersurface. This cation can equilibrate with a pair of asymmetrical species of similar stabilities (**5** ⇄ **4** ⇄ **5′**) [14], thus supporting the

5′ 4 5

suggestions of *Lee* [7] [10]. Nevertheless, this interpretation seemed to be incomplete. First, we do not understand why **1** and **2** should not collapse to the more stable 3-nortricyclyl cation **3** [15] [16]. Secondly, why should the secondary 5-norbornen-2-yl system, for which π-participation cannot be ruled out [9] [17], behave differently from structurally related homoallylic esters (*e.g.:* benzo-5-norbornen-2-yl [18], 5,6-dimethylidene-2-norbornyl [19], 5-bicyclo[2.2.2]octen-2-yl [20], 2-bicyclo[3.2.1]octen-7-yl [21], 3-cyclohexen-1-yl esters [22]), for which cyclopropylcarbinyl cationic intermediates have been invoked to explain the kinetics and products?

We now show that the solvolyses of *exo-* and *endo*-5-norbornen-2-yl brosylates can be adequately explained in terms of the 'free' cation intermediate **3** that equilibrates with symmetrical ion-pairs [23]. We have re-investigated the acetolyses of the *exo-* and *endo*-(2-D)-5-norbornen-2-yl brosylate (**6** and **7**) and report the product analyses for their buffered trifluoroethanolyses.



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Results. – The *endo-* and *exo*-(2-D)-5-norbornen-2-yl brosylates **6** and **7**, respectively, were prepared according to literature [6] [10]. Mass spectrometry (MS.) showed 98–99% deuteration; ^{1}H-NMR. and ^{2}H-{^{1}H}-NMR. spectra [24] *(cf. Fig. 5)* indicated that more than 95% of the label was at C(2).

Buffered trifluoroethanolysis (CF_3CH_2OH/CH_2Cl_2 1:1 + 1.2 equiv. pyridine, 25°) of **6** gave a mixture of volatile products in 98% yield, consisting of 6.2% of

Table. *Product and deuterium label distribution therein for the buffered trifluoroethanolyses and acetolyses of the brosylate* **6** *and* **7**[a])

Starting material					Bicyclic/tricyclic product ratio
X = OCH_2CF_2	**9**	**10**	**11**	**12**	
6 —[b])→	3.5%	3.5%	46.5%	46.5%	7:93
7 —[c])→	4.7%	3.3%	46%	46%	8:92
X = OAc	**13**	**14**	**15**	**16**	
6 —[d])→	3.8%	3.8%	46.2%	46.2%	7.5:92.5 9.5:90.5[e])
7 —[e])→	17.6%	5.4%	38.5%	38.5%	23:77 18:82[f])

[a]) Corrected for 98.5% deuteriation, as measured by MS. [b]) At 25°, CF_3CH_2OH/CH_2Cl_2 1:1 + 1.2 mol-equiv. pyridine. [c]) As [b]) but at 80°. [d]) At 25°, AcOH + 1.2 mol-equiv. AcOK. [e]) As [d]) but at 80°. [f]) As [d]) but at 118° [6].

2*exo*-(2,2,2-trifluoroethoxy)-5-norbornene (isotopomers **9** + **10**), 91.8% of 3-(2,2,2-trifluoroethoxy)nortricyclane (isotopomers **11** + **12**) *(cf. Table)* and 2% of minor compounds (less than 1% of norbornadiene). The products were separated by preparative GC.; their structures were deduced from their spectra and by comparison with the corresponding acetates [5–7] [10].

The ^2H-{^1H}-NMR. spectrum of the bicyclic ethers **9** + **10**, showed an equal distribution of the deuterium label at positions *endo*-C(2) and C(1) *(cf. Fig. 1A)*. If one considers the signal/noise ratio S/N = 360 (for 0.5 D) *(Fig. 1A)*, it appears that less than 0.3% of the deuterium atom is at any other position, corresponding to less than 2% of a rearrangement process scrambling all the H-atoms. MS. analysis of **9** + **10** [5b] confirmed the presence of 49.3 ± 1% D at C(2,3) and 49.3 ± 1% at C(1,4,7,5,6). The ^2H-{^1H}-NMR. spectrum of the tricyclic ethers **11** + **12** taken in presence of Eu(fod)$_3$ *(cf. Fig. 1B)* also showed an equal distribution of the label between positions C(1) and C(6).

Buffered trifluoroethanolysis (80°, 4 days) of the *endo*-brosylate **7** yielded a mixture of volatile products (97–98%) again consisting of compounds **9**–**12** (less than 1% of norbornadiene, *cf. Table*). These were separated by preparative GC. The ^2H-{^1H}-NMR. *(cf. Fig. 2A)* and the MS. of the bicyclic ethers **9** + **10** showed incomplete scrambling of the deuterium label between positions *endo*-C(2) and C(1) (83% rearrangement, *cf. Table*). However, in the tricyclic ethers **11** + **12** the label was found equally distributed between positions C(1) and C(6) *(cf. Fig. 2B)*. Considering the ratio S/N = 430 (for ~0.5 D) *(Fig. 2B)*, we can state that less than 0.3% of the deuterium atom in **11** + **12** is at any other site and less than 2% is distributed simultaneously at all the other positions.

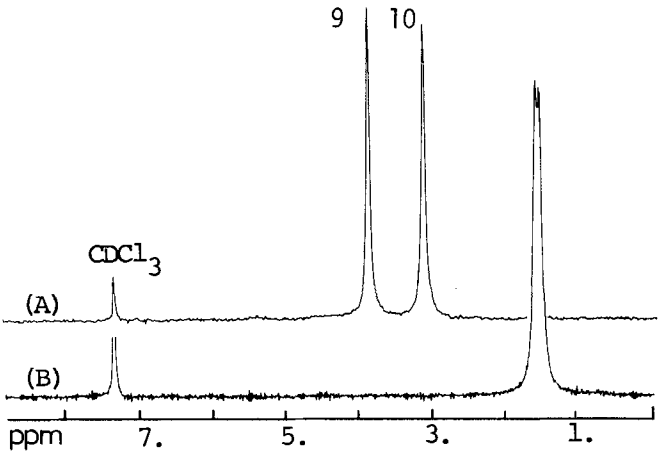


Fig. 1. *^2H-{^1H}-NMR. (CCl_4+ $CDCl_3$) spectra of (A)* **9**+**10** *and (B)* **11**+**12** (in presence of Eu(fod)$_3$) *obtained by trifluoroethanolysis of* **6** *at 25°.* Assignment was readily made on the basis of the 1:1 relation between ^1H and ^2H chemical shifts.

When the trifluoroethanolysis of unlabelled *exo*-brosylate **6′** was carried out in the presence of 1.5 mol-equiv. of pyridinium brosylate, we observed the formation of *ca.* 25% of 3-nortricyclyl brosylate **8** after one half-life period (*cf.* the common ion effect on the acetolysis of **6** [5a]).

The deuterium distribution observed in the above solvolyses contradicts the tritium label distribution reported by *Lee* [7] for the acetolysis of the *exo*-(3*exo*-T)-5-norbornen-2-yl brosylate. We have therefore repeated the acetolysis of **6** and **7** and analyzed the resulting acetates **13**–**16** *(cf. Table)* by our method.

The buffered acetolysis of **6** (0.5 M in AcOH, 1.2 mol-equiv. AcOK, 25°) yielded a mixture of volatile products (98% yield) containing the deuteriated bicyclic and tricyclic acetates **13**+**14** and **15**+**16** *(cf. Table),* which were separated

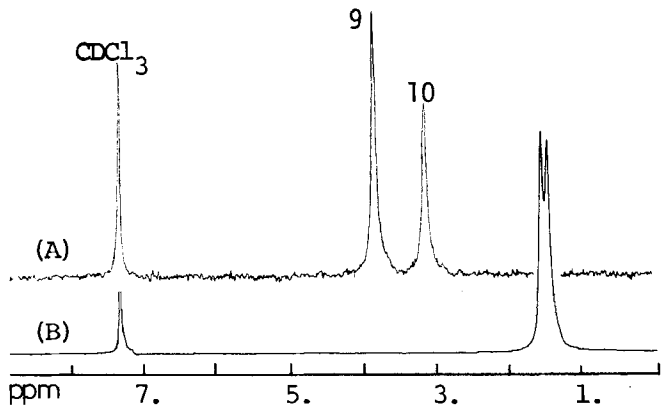


Fig. 2. *^2H-{^1H}-NMR. (CCl_4+ $CDCl_3$) of (A)* **9**+**10** *and (B)* **11**+**12** (in presence of Eu(fod)$_3$) *obtained by trifluoroethanolysis of* **7** *at 80°*

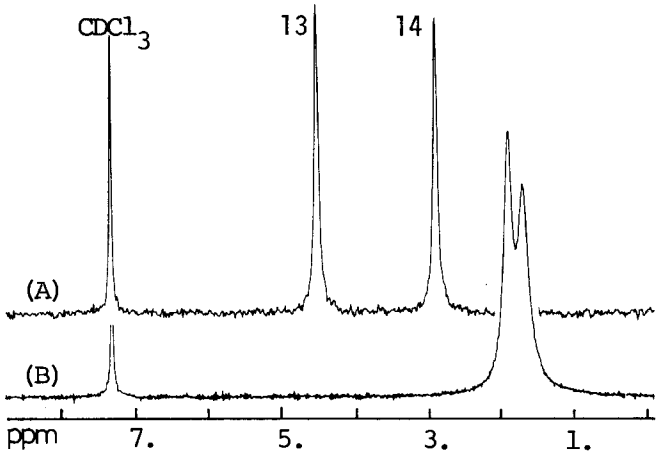


Fig. 3. *^{2}H-{^{1}H}-NMR. (CCl_4 + $CDCl_3$) of (A)* **13** + **14** *and (B)* **15** + **16** (in presence of Eu(fod)$_3$) *obtained by acetolysis of* **6** *at 25°*

by preparative GC. (less than 1% of norbornadiene). The ^{2}H-{^{1}H}-NMR. *(cf. Fig. 3A)* and the MS. of **13** + **14** showed complete scrambling of the deuterium label between *endo*-C(2) and C(1). Once again, the S/N ratio *(Fig. 3A)* demonstrates that less than 0.6% deuterium is at any other site. These results, again, are in complete disagreement with those obtained by *Lee* [7]. In the 3-nortricyclyl acetates **15** + **16**, the deuterium label *(cf. Fig. 3B)* was found almost equally distributed between C(1) and C(6) (S/N = 184; <0.6% D at any other position, 4% of D simultaneously at all other positions).

The buffered acetolysis of the *endo*-brosylate **7** (AcOH, 1.2 equiv. AcOK, 80°, 4 days) gave a mixture (96% yield) of the volatile acetates **13**–**16** (< 1% norbornadiene). The ^{2}H-{^{1}H}-NMR. *(cf. Fig. 4A)* and the mass spectra of **13**–**14** showed that 23–24% of the deuterium label had migrated from C(2) to C(1) (47% rearrangement). When the acetolysis of **7** was run at higher temperature (118°),

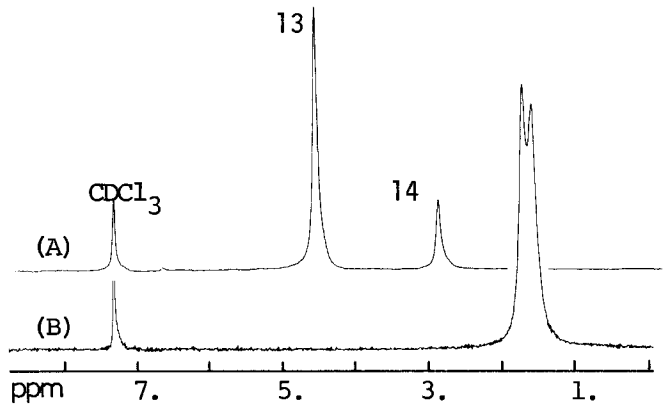
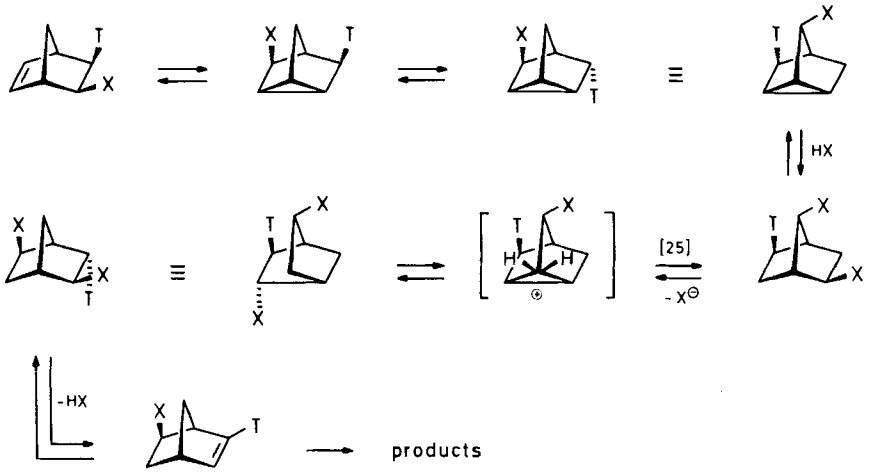


Fig. 4. *^{2}H-{^{1}H}-NMR. spectra of (A)* **13** + **14** *and (B)* **15** + **16** *obtained by acetolysis of* **7** *at 80°*

29–30% of the deuterium label was found at C(1) (60% of rearrangement [6]). Assuming S/N = 385 *(Fig. 4A)*, one can estimate that less than 0.6% of the deuterium atom has a position other than C(1) or C(2). The ^2H-{^1H}-NMR. spectrum (+ Eu(fod)$_3$) of the tricyclic acetates **15** + **16** showed complete scrambling of the label between positions C(1) and C(6) (*cf. Fig. 4B* [6]).

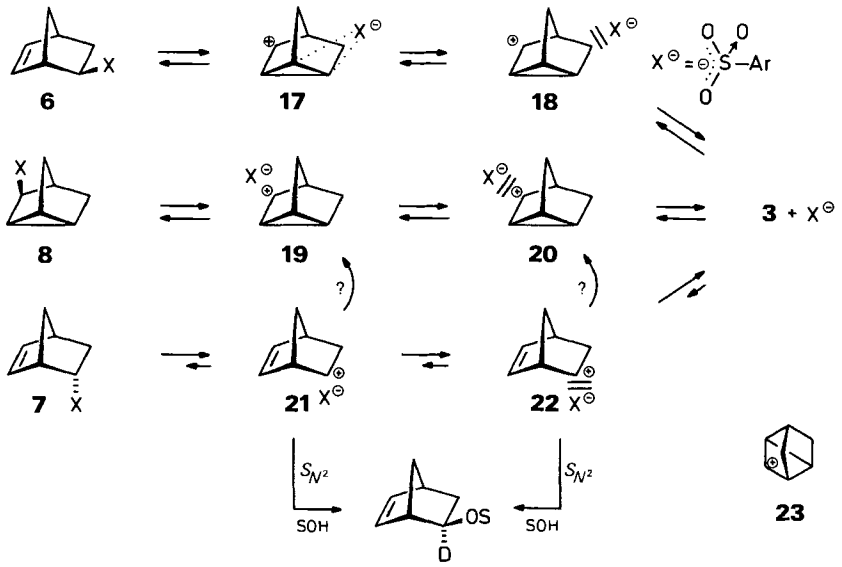
Within experimental error (see *e.g. Fig. 2B*, S/N = 430), our work confirms the absence of processes involving a) hydrogen migrations, b) elimination – addition (with formation of norbornadiene as intermediate) and c) addition – rearrangement – eliminations.

Discussion. – The discrepancies between our results and those of *Lee et al.* are difficult to explain. We have run several buffered acetolyses of **6** contaminated with various amounts of **7** under the conditions reported [7]. MS. analyses constantly showed a 50:50 distribution of the deuterium label between the positions C(2,3) and C(1,4,5,6,7) in the bicyclic acetates **13** + **14**. We observed that incomplete buffering could alter dramatically the distribution of the products due to the formation of norborna-2,5 and -2,7-diyl derivatives [25]. We found that substantial amounts of brosyl chloride (BsCl) used in the preparation of **6** and **7** could contaminate these esters if they were not crystallized with great care. Washing the crude brosylates with ether before recrystallization was necessary to ensure removal of all traces of this contaminant. It is possible, therefore, that buffering can become incomplete if some BsCl contaminates the brosylates under investigation. In that case, 5-norbornen-2-yl and 3-nortricyclyl derivatives can undergo addition-rearrangement-elimination processes [25]. One can envisage a label at C(3) migrating to C(6) in the 5-norbornen-2-yl acetate by such a process, *e.g.*:



The incomplete equilibration of the deuterium label between the positions C(2) and C(1) in the bicyclic ethers **9** + **10** (83% rearrangement at 80°) and acetates **13** + **14** (47% rearrangement at 80°, 60% at 118°) is best interpreted by invoking the contribution of a direct solvent attack (S_N2 with inversion) in competition with a S_N1 process. Solvent participation being larger with the more nucleophilic AcOH

than with CF_3CH_2OH [26], we expected a more advanced rearrangement in the latter. The larger bicyclic/tricyclic product ratio *(cf. Table)* in the acetolysis (23:77 at 80°) than in the trifluoroethanolysis of **7** (8:92 at 80°) agrees with our interpretation. Considering the portion of the acetate **13** which arises from direct S_N2 attack on **7** ((17.6–5.4)% = 12.2% of the total mixture **13–16**), the calculated bicyclic/tricyclic product ratio 12.3:87.7 is significantly larger than the acetate ratio measured for the acetolysis of **6** (9.5:90.5 at 80°) or **8** (8:92 at 80°). These differences can best be rationalized by invoking the intervention of several symmetrical ion-pairs **17–20** equilibrating with the 'free' 3-nortricyclyl cation (**3**), *e.g.*:



The tight ion-pair **17** is expected to yield exclusively 3-nortricyclyl derivatives upon quenching with the solvent (SOH), whereas **19** will generate *exo*-5-norbornen-2-yl products. The solvent-separated ion-pairs **18** and **20**, as well as the 'free' ion **3** are expected to form different mixtures of the tricyclic and bicyclic products upon quenching.

It has been claimed recently [13] that the cyclobutyl cation might be a relatively stable species [27] equilibrating with the cyclopropylcarbinyl cation in the gas phase. Our work does not support the intervention of the corresponding cyclobutyl derivative **23**. Ring strain arguments predict this species to be much less stable than **3**.

Conclusion. – If asymmetrical intermediates are formed during the buffered trifluoroethanolysis and acetolysis of *exo*-5-norbornen-2-yl brosylate they must equilibrate or collapse very rapidly to the more stable, symmetrical 3-nortricyclyl cation intermediate (and corresponding ion-pairs). There is no evidence for an energy barrier to the isomerizations of hypothetical 5-norbornen-2-yl cation intermediates (**1** ⇆ **2**) and/or to the isomerization of these species to the 3-nortricyclyl

cation (**1**⇆**3**, **2**⇆**3**) [16]. Thus, the 5-norbornen-2-yl/3-nortricyclyl system does not differ significantly from the other related homoallyl/cyclopropylcarbinyl systems [18–22].

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Experimental Part

General remarks. Melting points (m.p., not corrected), *Tottoli* apparatus. Mass spectra (MS.) in electron ionization mode, CEC 21-490 *Bell-Howell* spectrometer. ^{1}H-NMR. spectra. *Bruker* WP 80 CW, δ ppm (apparent multiplicity, *J* Hz, number of protons); *s* singlet, *d* doublet, *t* triplet, *qa* quadruplet, *m* multiplet, $\delta_{TMS} = 0.0$ ppm, br. broad. ^{2}H-{^{1}H}-NMR. spectra, *Varian* XL 100 (15.4 MHz, FT mode, ^{19}F resonance of C_6F_6 as external lock-signal), $CDCl_3$ (δ[ppm] 7.28) as internal reference. Eu(fod)$_3$ from *Willow Brook* Labs (Waukesha, Wisc., USA) was used without purification. Vapour phase chromatography (GC.), *Varian* Aerograph 90 P-3 (*Wilkens* Instruments and Research) or Fractovap 2400 V *(Carlo Erba);* integrator HP 3380 A *(Hewlett Packard).* Abbreviations: aq. aqueous, RT. room temperature, sat. saturated, TLC. thin layer chromatography, THF tetrahydrofuran; *i.V. in vacuo* (vacuum line), BsCl = *p*-bromobenzenesulfonyl chloride.

Exo-5-Norbornen-2-yl brosylate and acetate [5a], *endo*-5-norbornen-2-yl brosylate and acetate [6] and 3-nortricyclyl brosylate and acetate [28] were prepared according to literature.

Endo-*(2*exo-*D)-5-Norbornen-2-yl brosylate* (**7**) was prepared as reported [6] [10] by reduction of 5-norbornen-2-one [29] with $NaBD_4$ (> 98.5% D, *Fluka*) in dry THF, followed by esterification with BsCl/pyridine. M.p. 84–85° ([3]: 87°). – ^{2}H-{^{1}H}-NMR. ($CCl_4 + CDCl_3$): $\delta_D = 5.31$ ppm (see *Fig. 5*). – MS. (70 eV): 98–99% D_1.

Exo-*(2*endo-*D)-5-Norbornen-2-yl brosylate* (**6**), see [10]. M.p. 79.5–80.5°. – ^{2}H-{^{1}H}-NMR. ($CCl_4 + CDCl_3$): $\delta_D = 4.65$ ppm (see *Fig. 5*). – MS. (70 eV): 98–99% D_1.

Trifluoroethanolysis of **6**. The *exo*-brosylate **6** (2 g, 6.1 mmol), freshly distilled (CaO) pyridine (0.6 ml, 7.4 mmol), CH_2Cl_2 (6 ml) and freshly distilled (K_2CO_3, N_2) CF_3CH_2OH *(Fluka, puriss.)* were placed in a Pyrex tube that was sealed *i.V.* after complete degassing. After 4 days at 25 ± 1°, the mixture was poured into ice/water (20 ml) and extracted with ether (100 ml). The organic extract was washed successively with HCl 1N (3 × 20 ml) and sat. aq. $NaHCO_3$-solution. After drying ($MgSO_4$)

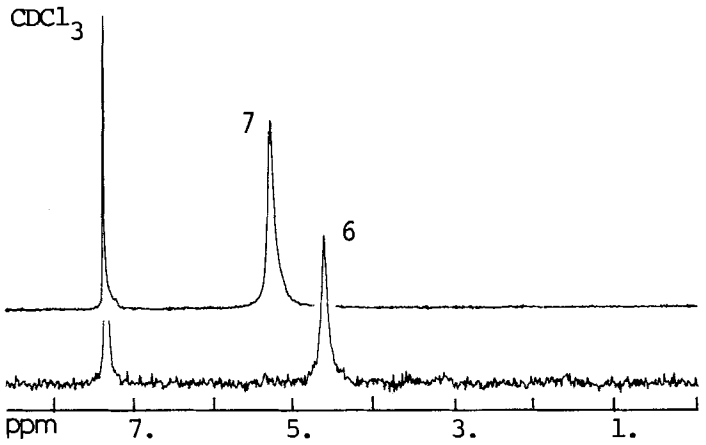

Fig. 5. *^{2}H-{^{1}H}-NMR. spectra of the* exo-*brosylate* **6** *and* endo-*brosylate* **7**

the solvent was removed under reflux, the residue was distilled *i.V.* Yield: 1.14 g (98%), colourless liquid (**8**+**9**+**10**+**11**); separation by preparative GC. (polyphenyl ether 20%, chromosorb WAW 60/80 mesh, 3.2 m × 8 mm, 110°, 120 ml/min H_2). The first fraction contained the (D_1)-2*exo*-(2,2,2-trifluoroethoxy)-norborn-5-enes **9**+**10**. – ^{1}H-NMR. (CCl_4): 5.98 (*m*, 1H); 5.86 (*m*, 1H); 3.85 (*qa*, $^3J_{HF}$ = 8.5 Hz, 2H); 3.58 (*m*, 0.5 H); 2.82 (*m*, 1.5 H); 1.8–1.26 (*m*, 4 H). – ^{2}H-{^{1}H}-NMR. (CCl_4 + $CDCl_3$), *cf. Figure 1A*.

The second fraction contained the (D_1)-3-(2,2,2-trifluoroethoxy)nortricyclanes **11**+**12**. – ^{1}H-NMR. ($CDCl_3$): 3.8 (*qa*, $^3J_{HF}$ = 8.5 Hz, 2 H); 3.69 (*m*, 1H); 2.01 (*m*, 1H); 1.86 (*m*, 1H); 1.5–1.0 (*m*, 5 H). – ^{2}H-{^{1}H}-NMR. (CCl_4 + $CDCl_3$), *cf. Figure 1B* and *Table*.

Trifluoroethanolysis of **7**. Same procedure as above, except that heating to 80° for 4 days was required for complete reaction. Product analysis, *cf. Table* and *Figure 2*.

Common ion effect on the trifluoroethanolysis of **6′**. The *exo*-brosylate **6′** (0.59 g, 1.8 mmol) in dry CH_2Cl_2 (5 ml) was added to a solution of pyridinium brosylate (0.8 g, 2.6 mmol) in CF_3CH_2OH (5 ml) and pyridine (0.079 g, 1 mmol). After stirring at 0° for 105 min (*ca.* 1 $\tau_{1/2}$) the reaction mixture was poured into ice/water (10 ml) and extracted with ether (50 ml). The organic phase was washed successively with HCl 1N (2 × 20 ml) and sat. aq. $NaHCO_3$-solution (2 × 20 ml). After drying ($MgSO_4$), the solvent was distilled off under reflux and the volatile solvolysis products eliminated *i.V.* The residue was a 1:1 mixture of **6**/**8** as shown by ^{1}H-NMR. and TLC. (SiO_2 + 10% $AgNO_3$, hexane/THF 60:40).

Acetolysis of **6**. Acetic acid (AcOH) (*Fluka*, p.a.) was heated under reflux for 12 h in presence of 10% (*v/v*) of freshly distilled acetic anhydride (*Fluka, p.a.*) and then distilled through a 60 cm *Hempel* column. The fraction b.p. 116.5–117.5° was collected and stored under N_2 after addition of 1% of acetic anhydride. The water content was checked periodically by the method of *Bruckenstein* [30]. Potassium acetate (AcOK) (*Merck, puriss.*) was dried at 180° for 4 days and stored under N_2. The brosylate **6** (2 g, 6 mmol) and a solution of AcOK 0.6M in AcOH (12.2 ml) were placed in a Pyrex tube that was sealed *i.V.* after complete degassing *i.V.* After 4 days at 25°, the solvolysis mixture was poured into ice/water (20 ml) and extracted with ether (100 ml). The organic extract was washed successively with H_2O (3 × 20 ml) and sat. aq. $NaHCO_3$-solution (3 × 20 ml). After drying ($MgSO_4$), the solvent was distilled off under reflux and the residue distilled *i.V.* Yield: 0.9 g (98%), colourless oil, containing **13**+**14**+**15**+**16** (> 98%) and norbornadiene (< 1%), separated by GC. (*Carbowax* 20M 15%, *Chromosorb* WAW 60/80 mesh silylated, 2.3 m × 8 mm, 120°, 120 ml/min H_2). Product analysis, *cf. Table* and *Figure 3*.

Acetolysis of **7** and **8**. Same procedure as above, 4 days at 80°. Product analysis, *cf. Table*, *Figure 4* and text.

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