108. The Acetolysis of *exo*- and *endo*-5,6-Dimethylidene-2-Norbornyl *p*-Bromobenzenesulfonates and of their Optically Active and Deuterium-Labelled Derivatives[1])

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Summary

The buffered (AcOK) acetolyses of *exo*- (**11**) and *endo*-5,6-dimethylidene-2-norbornyl brosylate (**12**) yielded *exo*-5,6-dimethylidene-2-norbornyl (**16**) and (3-methylidene-2-nortricyclyl)methyl acetates (**18**). *Endo*-5,6-dimethylidene-2-norbornyl (**17**) and 2-methylidene-3-tricyclo[3.2.1.$0^{3,6}$]octyl acetates (**20**) could not be detected. The titrimetric rate constants of the acetolysis of **11** ($k_{t(exo)} = 4.49 \pm 0.02) \cdot 10^{-5}$ s^{-1} at 25°, $\Delta H^{\neq} = 23.6 \pm 0.7$ kcal mol^{-1}, $\Delta S^{\neq} = 0.7 \pm 2$ calmol^{-1} K^{-1}) and **12** ($k_{t(endo)} = (1.9 \pm 0.08) \cdot 10^{-9}$ s^{-1} at 25°, $\Delta H^{\neq} = 27 \pm 1$ kcal mol^{-1}, $\Delta S^{\neq} = -8 \pm 2.5$ calmol^{-1} K^{-1}) were measured and compared with the polarimetric rate constants ($k_a/k_{t(exo)} = 6.8$ at 25°, $k_a/k_{t(endo)} = 1.0$ at 121°) of the buffered acetolyses of the opically active brosylates (+)-**11** and (+)-**12**. Neither a common-ion (KOBs) nor a special ion effect ($LiClO_4$) on $k_{t(exo)}$ could be detected, although external return might well intervene as some *exo*-5,6-dimethylidene-2-norbornyl tosylate (**21**) was formed upon solvolysis in the presence of KOTs. Acetolysis of (+)-**11** yielded completely racemized products, whereas (+)-**12** led to incomplete racemization. The buffered acetolysis of *exo*-(3*exo*-D)-5,6-dimethylidene-2-norbornyl brosylate (**24**) furnished (3*exo*-D)-(**26**: 37.5%), *exo*-(7*syn*-D)-5,6-dimethylidene-2-norbornyl (**27**: 37.5%) and [(5*anti*-D)-3-methylidene-2-nortricyclyl]methyl acetates (**28**: 25%). The acetolysis of *endo*-(2*exo*-D)-5,6-dimethylidene-2-norbornyl brosylate (**25**) yielded (2*endo*-D)-(**29**: 54%), *exo*-(1-D)-5,6-dimethylidene-2-norbornyl (**30**: 36%) and [(6-D)-3-methylidene-2-nortricyclyl]methyl acetates (**31**: 10%). Product analysis and deuterium label distribution was established by a combination of GC., ^{1}H-NMR., ^{2}H-{^{1}H}-NMR. and MS. techniques. The results are rationalized by invoking anchimerically assisted ionization of the *exo*-brosylate **11** to sym-

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[1]) Preliminary report: [1]. This work has been reported in part to the meeting of the 'Société suisse de chimie' in Bern, oct. 1977.

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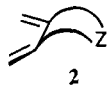
metrical ion-pairs (cyclopropylcarbinyl cation intermediates) which undergo internal (and probably also external) return. Acetolysis of the *endo*-brosylate **12** is not anchimerically assisted and leads initially to non-symmetrical ion pairs. These evolve to symmetrical ion pair intermediates or, to a minor extent, are intercepted by solvent.

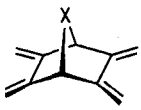
Introduction. – Transannular interactions between a s-*cis*-butadiene function and a remote group Z facing the 'front' of the diene, as depicted in **1**, have been studied extensively by spectroscopic and chemical methods. In these cases Z was an unsaturated function [2] [3], a heteroatom [3] [4], an anionic [5] or a cationic function [6]. Evidence for homoconjugative and hyperconjugative interactions [7] between the back-to-back oriented exocyclic s-*cis*-butadiene chromophores in the tetraenes **3** (X=CH_2 [8], O [9], CH_2–CH_2, CH=CH [10]) has been found in the UV. absorption spectra and the PE. spectra [11][4]).

1
'front'



2
'back'

The trienes **4** (X=CH_2, O) are less reactive than the corresponding tetraenes **3** and their parent dienes **5** toward strong dienophiles, probably because of changes in the electronic properties of the dienes [14]. This is also true for the *Diels-Alder*



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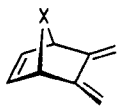

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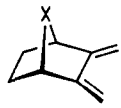

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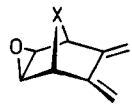

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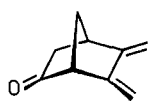

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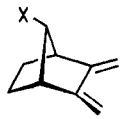
reactivity of the monoadducts of **3**, which makes the tetraenes valuable synthons for the preparation of polycyclic, polyfunctional systems [15] [16]. We have also shown that the *exo*-epoxide groups in **6** (X=CH_2, O) exert a significant rate retarding effect on the *Diels-Alder* reactivity of the diene which was attributed to electronic factors rather than to geometry and/or strain factors [17]. Homoconjugative and hyperconjugative interaction between the carbonyl and diene functions of **7** were evidenced by UV. [18] and ^{13}C-NMR. spectroscopy [19]. These interactions are probably responsible for the regioselectivity observed in the cycloadditions of **7** [20].



8
k (25°, AcOH): $\sim 8.8 \cdot 10^{-10}$

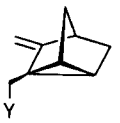
9
$\sim 2.6 \cdot 10^{-3}$

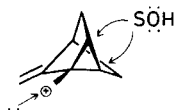
10
X=OBs (brosylate) $\sim 6 \cdot 10^{-14}$ s^{-1} [21]

4) For other systems in which two exocyclic s-*cis*-butadiene groups are juxtaposed in a non-conjugated fashion, see *e.g.* [12] [13].

Tanida et al. [21] have reported the buffered acetolysis of *anti*-2,3-dimethylidene-7-norbornyl *p*-bromobenzenesulfonate (brosylate **8**). This reaction was shown to proceed *via* a secondary carbenium ion intermediate and to be assisted somewhat by the s-*cis*-butadiene unit (system **2**). In this case, symmetry impedes a LUMO (carbenium ion) – HOMO (diene) stabilizing interaction, a probable explanation for the much lower S_N1 reactivity of **8** relative to that of **9** [21].

We now present a study on the solvolysis of *exo*- and *endo*-5,6-dimethylidene-2-norbornyl brosylates (**11**, **12**), isomeric with **8** but not subject to the above symmetric constraint[5]), and which closely resemble 5-norbornen-2-yl [23] and benzo-5-norbornen-2-yl brosylates [24] in their solvolytic behaviour. Using kinetic and product analysis as well as deuterium label distribution, we show that the intermediacy of the symmetrical cyclopropylmethyl cation **13** and the corresponding ion-pairs best account for the observations.





Y =				
OBs	**11**	**12**	**22**	**13**
OH	**14**	**15**	**19**	
OAc	**16**	**17**	**18**	
OTs	**21**		**23**	

Results. – The *exo*-5,6-dimethylidene-2-norbornyl brosylate **11** was obtained by esterification (BsCl/pyridine) of the corresponding alcohol **14** [18]. The ketone **7**, prepared by *Collins* oxidation of **14** (yield 75%), was reduced with $LiAl(OMe)_3H$ [25] to a 98:2 mixture of the *endo*- and *exo*-alcohols **15** and **14** respectively. The structure of **15** was deduced from its spectra [19] and by comparison with other 2,3-dimethylidenenorbornane derivatives [26]. The *endo* position of the hydroxyl group followed from the vicinal coupling constants $^3J_{H-C(2),H-C(1)} = 3.2$ Hz, $^3J_{H-C(2),Hexo-C(3)} = 10$ Hz and $^3J_{H-C(2),Hendo-C(3)} = 3$ Hz [27]. The brosylate **12** was prepared by esterification (BsCl/pyridine [28]) of **15**.

The buffered (AcOK) acetolysis of **11** at 25° yielded a mixture of volatile products (yield 98%) consisting of the bicyclic and tricyclic acetates **16** and **18**, respectively ($75 \pm 1 : 25 \pm 1$) and less than 2% of olefinic compounds. At 100°, the acetolysis of **11** yielded roughly the same mixture (**16/18** 77:23). The acetates **16** and **18** were stable under the above conditions; their yield and ratio were independent of the initial concentration of **11** (0.1 to 0.5 M), of the excess of AcOK (1.1 to 1.5 mol-equiv.) and of the degree of conversion (0.2 to 15 $\tau_{1/2}$). The structure of **16** was deduced from its spectra [19] and by comparison with the acetate obtained by acetylation of the alcohol **14**. The structure of the tricyclic acetate **18** was deduced from its spectra (see exper. part) and by comparing the latter with those of 6-methyl-5-methylidene-3*anti*-nortricyclanol (obtained by

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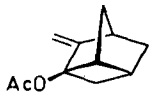
[5]) For cases of π-participation of an exocyclic methylidene group on a homoconjugated cationic intermediate, see *e.g.* [22].

$LiAlH_4$ reduction of the epoxydiene **6** ($X=CH_2$)) and 6-chloromethyl-5-methylidene-3*anti*-nortricyclanol [29] (obtained by HCl addition to **6**).

The buffered acetolysis of the *endo*-brosylate **12** was slower than that of **11** (see *Table 1*). After 4 days at 100°, a volatile mixture (yield 94%) consisting of the acetates **16** and **18** (90:10) and less than 2% of the triene **4** ($X=CH_2$) was obtained. No trace of the *endo*-acetate **17** nor of the cyclobutyl derivative **20** could be detected (<0.5% GC.). The ester **17** was stable under the conditions of the acetolyses of **11** and **12** and was prepared independently by acetylation of the corresponding alcohol.



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The titrimetric rate constants of the acetolyses of **11** and **12** *(Table 1)* were measured by a UV. spectrometric technique [30]. A ratio $k_{t(exo)}/k_{(endo)} \cong 23{,}600$ was obtained at 25° by *Arrhenius* extrapolation of the rate constant for the *endo* derivative. In order to evaluate the importance of external return [31] in the solvolysis of **11** we measured the rate constants as a function of the concentration of added potassium brosylate *(Table 2)*. No rate retardation but a slight rate increase was observed owing to the increase of the ionic strength of the medium [32]. The rate followed the linear relationship: $k=k^\circ\,(1-b[KOBs])$ with $b=14.6$ and $k^\circ=4.52\pm0.07\cdot10^{-5}\ s^{-1}$ at 25.1°. This k_0 value was comparable to the titrimetric rate constant $k_t^\circ=4.55\pm0.02\cdot10^{-5}\ s^{-1}$ interpolated from the values reported in *Table 1*. Thus, no common ion effect is detectable *kinetically* for concentration of KOBs up to $5.6\cdot10^{-3}$ M (higher concentration could not be used with our measurement technique).

Table 1. *Titrimetric rate constants* k_t *and activation parameters of the buffered* (1.18 mol-equiv. AcOK) *acetolyses of the brosylates* **11** *and* **12** ($2.1\cdot10^{-3}$ M)

11	T [°C]	22.1	24.6	27.2	29.7	35.7	39.8	45.0	50.0	±0.05 Interpolation: 25°
	$k_t^*10^5$ [s^{-1}]	2.94	4.16	5.90	9.7	18.4	31.3	58.8	103	4.49
		±0.05	±0.05	±0.05	±0.05	±0.5	±0.5	±0.5	±5	±0.02
		$A=2.5\cdot10^{13}\ s^{-1}$, $\Delta H^{\neq}=23.6\pm0.7$ kcal · mol^{-1}, $\Delta S^{\neq}=0.7\pm2.0$ calmol^{-1} K^{-1}								
12	T [°C]	100.4	120.3	135.1						25°
	$k_t^*10^5$ [s^{-1}]	2.33	15.5	55.6						0.00019
		±0.1	±0.7	±0.5						±0.000008
		$A=4\cdot10^{11}\ s^{-1}$, $\Delta H^{\neq}=27\pm1$ kcal · mol^{-1}, $\Delta S^{\neq}=-8\pm2.5$ calmol^{-1} K^{-1}								

Table 2. *Titrimetric rate constants of the buffered* (1.18 mol-equiv. AcOK) *acetolyses of* **11** (2.1^*10^{-3} M) *in presence of added salts*

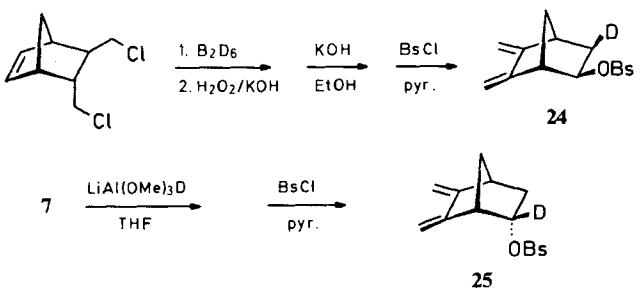
[KOBs]*10^3 [M]	0.796	1.49	2.37	2.88	5.6		$b=14.6\ M^{-1}$
k^*10^5 [s^{-1}]	4.56	4.63	4.71	4.69	4.89	at 25.1°	$k^\circ=4.52\pm0.07^*10^{-5}\ s^{-1}$
[$LiClO_4$]*10^3 [M]	1.10	5.50	10.95	16.42	21.90		$b'=29.0\ M^{-1}$
k^*10^5 [s^{-1}]	4.56	5.17	5.83	6.6	7.27	at 24.8°	$k^\circ=4.43\pm0.07^*10^{-5}\ s^{-1}$

Nevertheless external return could be detected by anion exchange. When **11** was acetolyzed for *ca.* one half-life (1 h, 35°) in the presence of 4 mol-equiv. of potassium *p*-toluenesulfonate (KOTs), a mixture of 35% **11**+15% of the corresponding tosylate **21** [δ_H=7.38 (*d*, 8 Hz, 2 H), 7.85 (*d*, 8 Hz, 2 H), 2.45 (*s*); *cf.* **11**: δ_H=7.78 (*m*, 4 H) in $CDCl_3$)] and 50% of the acetates **16**+**18** was obtained. Since the amount of **21** formed under these conditions is considerable, failure to observe the common ion-effect *kinetically* must be attributed to the small concentrations of KOBs used in these experiments. The tricyclic brosylate **22** and tosylate **23** could not be detected.

No special-salt effect [3] [33] [34] could be detected in the acetolysis of **11** in the presence of $LiClO_4$. A linear relation $k=k^\circ(1+b'[LiClO_4])$ with $b'=29$ and $k^\circ=4.43\pm0.07\cdot10^{-5}$ s^{-1} was observed at 24.8° (k_t° interpolated from the values in *Table 1:* $4.37\pm0.02\cdot10^{-5}$ s^{-1}) (see *Table 2*).

In order to gather more information about the mechanistic details of the solvolyses of **11** and **12** and about the possible π-participation of the 'back' of the s-*cis*-butadiene function in these reactions, we investigated the buffered acetolyses of the optically active brosylates (+)-**11** and (+)-**12** [35]. Acetolysis (1.15 mol-equiv. AcOK, 25°) of (+)-**11** gave a mixture of completely racemized acetates **16**+**18**, whereas the acetolysis (121°) of (+)-**12** yielded partially racemized products. The polarimetric rate constants k_a were measured in acetic acid *(Table 3).* A relatively high rate constant ratio $k_a/k_t=6.8$ (25°) was obtained for (+)-**11**, whereas for (+)-**12** $k_a/k_t=1.0$ (121°).

In order to limit the number of possible racemization mechanisms we studied the deuterium label distribution in the bicyclic and tricyclic acetates arising from the buffered acetolyses of *exo*-(3*exo*-D)-5,6-dimethylidene-2-norbornyl brosylate (**24**) and *endo*-(2*exo*-D)-5,6-dimethylidene-2-norbornyl brosylate (**25**). These esters were prepared according to the following scheme.



The *exo*−C(3) position of the deuterium atom in **24** was expected from the mode of formation [36] and by analogy with the synthesis of *exo*-(3*exo*-D)-5-norbornen-2-ol [37]. It was confirmed by ^{1}H-NMR. *(Fig. 1):* the signal at δ_H=2.03 ppm of H*exo*−C(3) and the vicinal coupling $^3J_{H-C(2),Hexo-C(3)}$ were absent. The ^{2}H-{^{1}H}-NMR. spectrum [23] *(Fig. 2)* showed one single peak at δ_D=2.03 ppm and established (signal/noise ratio, S/N=65) that less than 3% of the deuterium atom was at a position other than C(3) (>98% D_1 by MS.). The

exo–C(2) position of the deuterium atom in **25** was predicted from the mode of formation of the corresponding alcohol. It was confirmed by ^{1}H-NMR. (disappearance of the signals at $\delta_H = 4.2$ ppm in **15**, $\delta_H = 5.2$ ppm in **12** and the corresponding $^3J_{H-C(2),H-C(1)}$ couplings, see *Fig. 3*). The ^{2}H-{^{1}H}-NMR. spectrum *(Fig. 4)* showed a single line at $\delta_D = 5.2$ ppm and suggested (S/N = 33) that less than 6% of the deuterium label is at a position other than C(2).

Buffered (1.2 mol-equiv. AcOK, 25°) acetolysis of **24** yielded the acetates **26**, **27** and **28**, and **25** (100°) the acetates **29**, **30** and **31** *(Table 4)*. After preparative GC. separation of the bicyclic and tricyclic esters, the deuterium distribution was analyzed by ^{2}H-{^{1}H}-NMR. and MS.

The ^{2}H-{^{1}H}-NMR. spectrum of the bicyclic acetates **26**+**27** showed only two signals of similar intensity corresponding to D*exo*–C(3) and D*syn*–C(7).

Table 3. *Polarimetric rate constants* k_a *of the buffered* (1.15 mol-equiv. AcOK) *acetolyses of* (+)-**11** *and* (+)-**12** *and extent of racemization in the product* **16**

	T [°C]	k_a*10^5 [s^{-1}]	k_t*10^5 [s^{-1}]	k_a/k_t	Conc. [M]	Expected $[\alpha]_{365}^{25}$[a] without racemization[b]	Observed $[\alpha]_{365}^{25}$ After > 15 $\tau_{1/2}$	Racemization
(+)-**11**	25.0	30.6 ±0.7	4.49 ±0.05	6.8	0.107	−3.140 ±0.002	±0.002	99–100%
(+)-**12**	121.0	16.6 ±0.3	16.6 ±0.7	1.0	0.021	±0.630 ±0.002	±0.030 ±0.002	94–96%

a) Obtained by measuring $[\alpha]_{365}^{25}$ of (+)-**16** in presence of 1.15 equiv. of AcOK, 1 equiv. of KOBs in AcOH. (+)-**16** was not racemized under the conditions of the acetolyses after 15 $\tau_{1/2}$.

b) Assuming 100% **16** in the product.

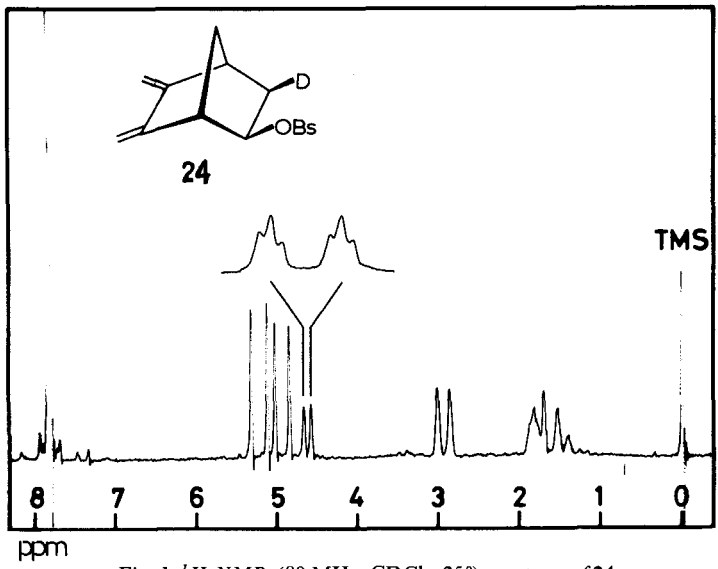
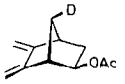
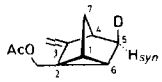
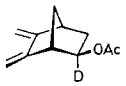
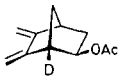
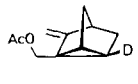


Fig. 1. *^{1}H-NMR.* (80 MHz, $CDCl_3$, 25°) *spectrum of* **24**

Table 4. *Products obtained from the acetolyses of the deuteriated brosylates* **24**, **25** (± 1%)

Brosylate	Products			Racemization[a])
24 solvolyzed at 25°				100%
	26 37.5%	**27** 37.5%	**28** 25%	
25 solvolyzed at 100°				81–82%
	29 54%	**30** 36%	**31** 10%	

[a]) Considering formation of the intermediate **13** without further scrambling.

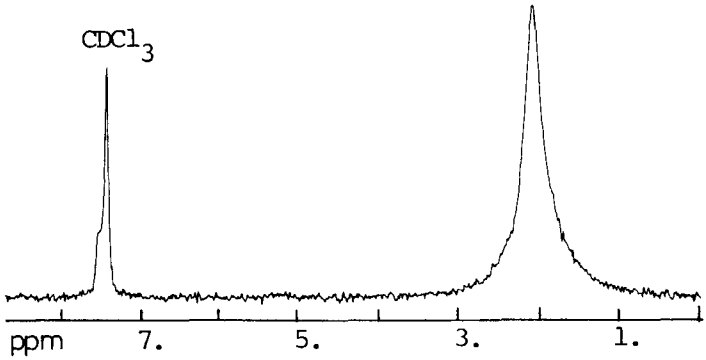


Fig. 2. ^2H-{^1H}-*NMR.* ($CCl_4/CDCl_3$) *spectrum of* **24** (S/N = 65)

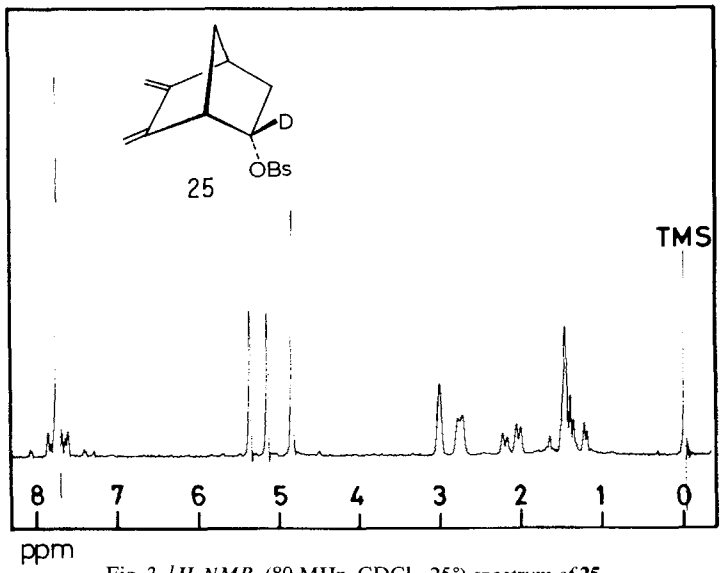


Fig. 3. ^1H-*NMR.* (80 MHz, $CDCl_3$, 25°) *spectrum of* **25**

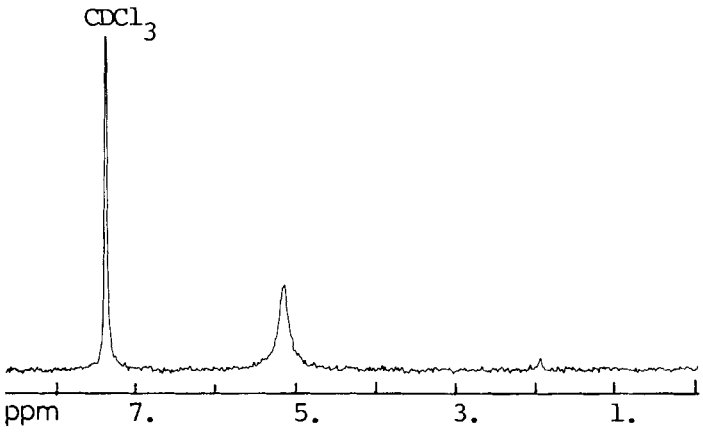
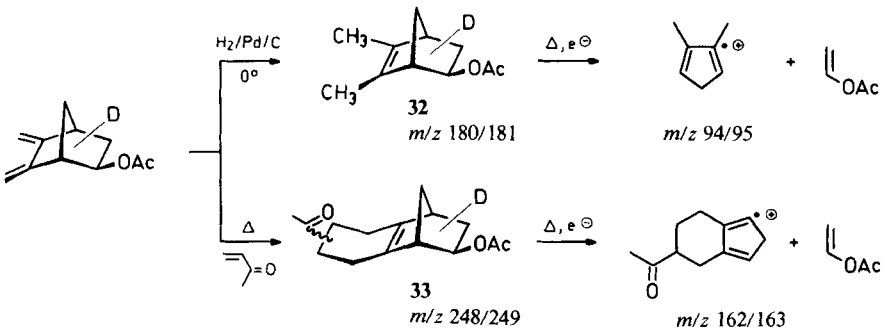


Fig. 4. ^2H-{^1H}-*NMR.* ($CCl_4/CDCl_3$) *spectrum of* **25** (S/N = 33)

Since the S/N ratio is 35 *(Fig. 5A)* less than 1.5% of the deuterium label can occupy a position other than those stated above. The ^2H-{^1H}-NMR. spectrum of the tricyclic acetate **28** displayed only one signal characteristic of D*anti*–C(5 or 7). With a S/N = 60 *(Fig. 5B)*, less than 2% of the deuterium label is elsewhere. No splitting of the deuterium signal of **28** could be observed in the presence of Eu(fod)$_3$. The ^2H-{^1H}-NMR. spectrum of the bicyclic acetates **29** + **30** arising from the acetolysis of **25** showed two signals of different intensities attributed to D*endo*–C(2) and –C(1) (**29**/**30** 60 ± 5 : 40 ± 5, *Fig. 6A*, S/N = 65). The ^2H-{^1H}-NMR. spectrum of the tricyclic acetate **31** displayed only one signal, even in the presence of Eu(fod)$_3$ (*Fig. 6B*, S/N = 25).



Partial catalytic hydrogenation of the dienes **26** + **27** and **29** + **30** yielded mixtures composed mostly of the corresponding *exo*-5,6-dimethyl-5-norbornen-2-yl acetates **32**[6]) (98–99% D_1 by MS.). When heated with excess methyl vinyl ketone, the dienes **26** + **27** and **29** + **30** yielded mixtures of the corresponding *Diels-Alder* adducts **33** [20]. The deuterium label distribution between positions C(2,3) and

[6]) 5,6-Dimethyl-5-norbornen-2*exo*-ol is a constituent of East Indian sandalwood oil [38]. Partial hydrogenation (Pd/C, pentane) of **14** constitutes a simple synthesis of this natural compound.

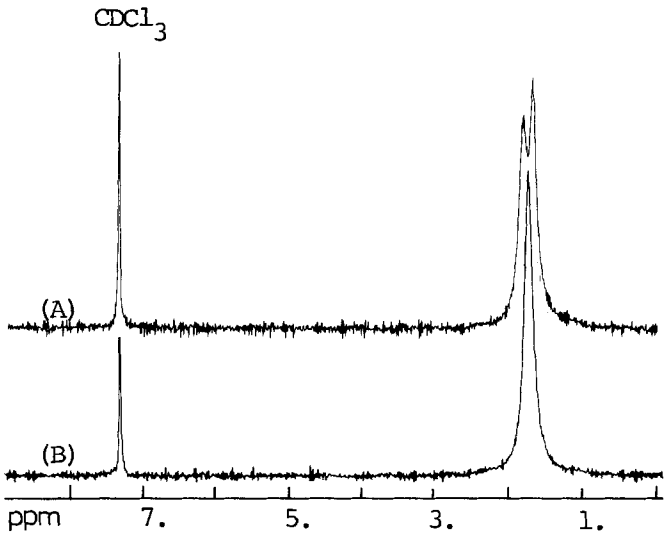


Fig. 5. *^2H-{^1H}-NMR.* (C_6F_6, 30°) *of (A)* **26**+**27**, *(B)* **28**

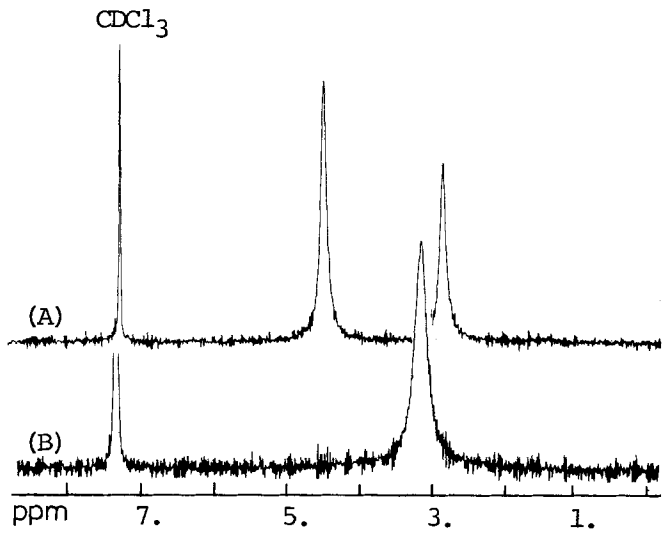


Fig. 6. *^2H-{^1H}-NMR.* (C_6F_6, 30°) *of (A) the bicyclic acetates* **29**+**30**, *(B)* (in presence of $Eu(fod)_3$) *the tricyclic acetate* **31**

C(1,4,5,6,7) of the norbornenyl derivatives **32** and **33** could be determined by MS. [39] more accurately than by ^{2}H-{^{1}H}-NMR. of the corresponding dienes **26**+**27** and **29**+**30**. These measurements (average values of 20 spectra) confirmed a 50:50 acetate ratio **26/27** (100% rearrangement) arising from the acetolysis of the *exo*-brosylate **24** (at 25°) and gave a product ratio of 59.5/40.5 for **29/30** arising from the *endo*-isomer **25** (at 100°) *(Table 4).*

Discussion. – The titrimetric and polarimetric rate constants (*Tables 1, 3* and *5*), the competitive formation of bicyclic (homoallyl) and tricyclic (cyclopropylcarbinyl) acetates **16**, **18** and the deuterium label distribution *(Table 4)* for the buffered acetolysis of deuteriated brosylates **24** and **25** demonstrate that the *exo*- and *endo*-5,6-dimethylidene-2-norbornyl brosylates (**11**, **12**) closely resemble the *exo*- and *endo*-5-norbornen-2-yl, and the *exo*- and *endo*-benzo-5-norbornen-2-yl brosylates in their solvolytic behaviour *(Table 5)*. The rate ratio $k_{a(exo)}/k_{a(endo)}$ reaches a 'record value' of 1.6×10^5 for **11**/**12**. This suggests that π-participation in the solvolysis of **11** is at least as important as in the case of its benzo analogue *(Table 5)* (steric hindrance to ionization of the *endo*-ester **12** should not be larger than that of its benzo analogue).

In our opinion, the results are best interpreted by anchimerically assisted ionization (k_Δ) of the *exo*-brosylate **11**, leading to symmetrical ion-pairs [31] [47], *e.g.*: **34**–**37** and **13** *(Mechanism 1)*. The ion-pairs undergo internal (and probably also external) return and give 99–100% racemic bicyclic acetate **16**. If asym-

Mechanism 1

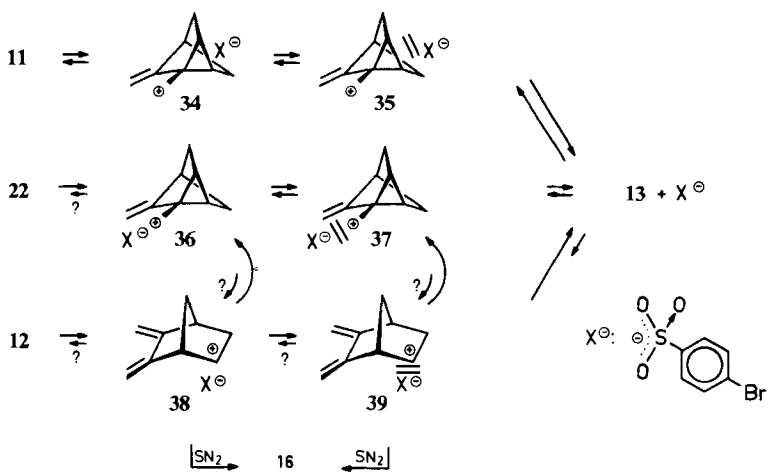


Table 5. *Kinetic data of the buffered acetolyses of secondary brosylates* (X = OBs) *at 25° [s^{-1}] unless otherwise stated*

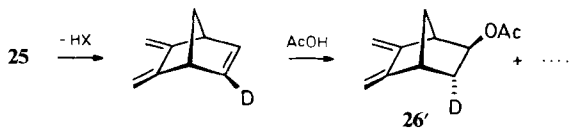
					
$k_{t(exo)}$	$8.82 \cdot 10^{-5}$ [40]	$4.13 \cdot 10^{-5}$ a)	$4.49 \cdot 10^{-5}$	$7.47 \cdot 10^{-6}$ [42]	$1.71 \cdot 10^{-7}$ [44]
$k_{t(endo)}$	$2.52 \cdot 10^{-7}$ [40]	$5.7 \cdot 10^{-9}$ [41]	$1.9 \cdot 10^{-9}$	$1.0 \cdot 10^{-9}$ [42]	
$k_a/k_{t(exo)}$	3.46 [45]	2.7 [46]	6.8	4.16 [43]	
$k_a/k_{t(endo)}$	~1.0 (75°) [45]		1.0 (100°)	1.0 (100°) [43]	
$k_{a(exo)}/k_{a(endo)}$	1,211	19,560 b)	160,700	31,075	

a) This work; [41]: $4.5 \cdot 10^{-5}$ s^{-1}.
b) Assuming $k_a/k_{t(endo)} = 1.0$.

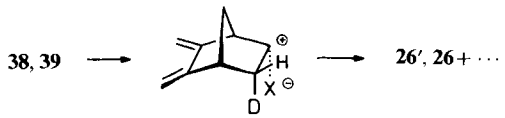
metrical ionized species are present, they must equilibrate more rapidly than they are quenched by the solvent. On the other hand, ionization of the *endo*-brosylate **12** is not anchimerically assisted (k_s) and first leads to non-symmetrical ion-pairs (**38**, **39**, *Mechanism 1*), which are then mainly converted to symmetrical ion-pair intermediates. The incomplete racemization as well as the partial equilibration of the deuterium label between positions C(2) and C(1) in the bicyclic acetates **29**+**30** is best interpreted by invoking the contribution of direct solvent attack (S_N2 with inversion). The larger bicyclic/tricyclic product ratio **16**/**18** observed for the acetolysis of **12** compared with that of the acetolysis of **11** confirms this hypothesis. Furthermore, the slightly negative activation entropy $\Delta S^{\neq} = -8 \pm 2$ e.u. measured for the acetolysis of **12** agrees with a tighter transition state in this reaction than in the acetolysis of **11** ($\Delta S^{\neq} = 0.7 \pm 2.5$ e.u.).

The different extents of racemization, as measured polarimetrically (94–96%) and evaluated from the deuterium label distribution (81–82%), might be due to the fact that acetolysis of (+)-**12** was run at higher temperature (121°) than that of **25** (100°). By analogy with the buffered acetolysis of *endo*-5-norbornen-2-yl brosylate [23], we expect a higher degree of racemization at higher temperature (the acetolysis of **25** at 121° or of (+)-**12** at 100° was not carried out because of lack of material). It cannot be excluded that more than one scrambling process intervenes in the racemization of the products with partial equilibration of positions C(2) and C(1) (and C(3) and C(7)). Elimination of *p*-bromobenzenesulfonic acid (HX) with formation of 5,6-dimethylidene-2-norbornene, followed by addition of AcOH in such a way as to avoid the formation of symmetrical ionized species such as **13**, **34**–**37** (probable in buffered AcOH, see *e.g.*: [48]), can be considered. Such a mechanism would generate (3-D)-acetate **26′** *(Mechanism 2)*. The ^{2}H-{^{1}H}-NMR. spectrum of **29**+**30** (*Fig. 6A*, S/N = 65) shows that less than 2% of **26′** is present, which gives little support for this mechanism. Hydrogen migration from C(3) to C(2) in the asymmetrical ion-pairs **38** and **39** *(Mechanism 3)* would also lead to racemized product with incomplete equilibration of the deuterium label between C(3) and C(7). Again, the ^{2}H-{^{1}H}-NMR. spectrum *(Fig. 6A)* shows that *mechanism 3* plays a minor role if any, since less than 2% of each of the 4 possible *exo*-(3- and 7-D)-5,6-dimethylidene-2-norbornyl acetates contaminate **29** and **30**.

Mechanism 2

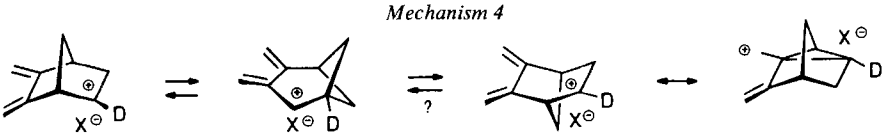


Mechanism 3



According to *mechanism 1*, the tight ion-pair **38** and the solvent separated ion-pair **39** could give the symmetrical intermediates **36** and **37**, respectively, by 'migration' of the counter-ion ($X^- = BrO^-$), or lead to the 'free' cation **13**. An irreversible rearrangement of **38** and **39** to **34** and **35**, respectively, can occur *via* a *Wagner-Meerwein* migration of $\sigma C(1,7)$ bond *(Mechanism 4)*. This alternative cannot be ruled out with our data.

Mechanism 4



The yield of the acetate **16** resulting from direct S_N2 attack on **12** (18–19% of the total product mixture at 100°), corresponds to a bicyclic/tricyclic acetate ratio of *ca.* 72:10, which is significantly larger than the ratio **16/18** of 77:23 measured for the buffered acetolysis of **11** at 100°[7]). These differences can best be rationalized by invoking the intervention of several symmetrical ion-pairs **34–37** *(Mechanism 1)* in equilibrium with the 'free' cyclopropylcarbinyl cation **13**. The tight ion-pair **34** is expected to yield exclusively tricyclic acetate **18** upon quenching with the solvent (SOH), whereas **36** should generate the racemized *exo*-acetate **16**. The solvent separated ion-pairs **35** and **37**, as well as the 'free' ion **13** are expected to form different mixtures of tricyclic/bicyclic products upon quenching. Equilibration of these carbocationic intermediates is competitive with their quenching with acetic acid and the brosylate anion.

Conclusion. – The solvolytic behaviour of *exo*- and *endo*-5,6-dimethylidene-2-norbornyl brosylates (**11**, **12**) closely resembles that of *exo*- und *endo*-5-norbornen-2-yl and *exo*- and *endo*-benzo-5-norbornen-2-yl brosylates. The 'back' of an exocyclic diene can assist the formation of a homoconjugated carbenium ion. This is confirmed by the relatively high polarimetric rate constant ratio $k_{a(exo)}/k_{a(endo)} = 160, 700$ measured for the buffered acetolysis of the brosylates (+)-**11**/(+)-**12**. If asymmetrical, bicyclic homoallyl cations are formed during the solvolysis of the *exo*-brosylate **11**, they must equilibrate or collapse very rapidly to the more stable, symmetrical tricyclic cyclopropylcarbinyl (and corresponding ion-pairs). There is no evidence for the intervention of tricyclic cyclobutyl cations.

We thank the *Swiss National Science Foundation* (FN. 2.446-0.75 and F. 2.648-0.76) and the *Stipendienfonds der Basler Chemischen Industrie* for generous financial support. We are grateful also to Mr. *J.P. Saulnier*, University of Geneva, for technical assistance in the measurements of the ^{2}H-NMR. spectra and to Mr. *H. Serra*, *N.M. Lan* and Dr. *J. McGarrity* for the MS. measurements.

[7]) When the tricyclic alcohol **19** was treated with BsCl/pyridine (0°) [28] or when its lithium alcoholate was quenched with BsCl in THF at 0°, only the corresponding bicyclic and tricyclic chlorides were isolated. Attempts to prepare the tricyclic brosylate **22** with *p*-bromobenzenesulfonic anhydride in CCl_4/pyridine at 0° only led to **11**. Simple thermochemical arguments [49] [50] suggest that **22** must be 2–3 kcal/mol less stable than **11**. This difference in stability might be responsible for the relatively high solvolytic reactivity of **22**. Perhaps its enhanced reactivity is partly due also to the selective formation of ion-pairs **36** and **37**, assumed to be more stable than **34** and **35**.

Experimental Part

General Remarks. Melting points (m.p.) and boiling points (b.p.) (not corrected), *Tottoli* apparatus. IR. spectra ($\tilde{\nu}$ [cm^{-1}]), *Beckman* IR-20 A and *Beckman* IR-4230 spectrometers. UV. spectra, *Pye Unicam* SP 1800 and *Carl Zeiss* RPQ 20 A/c instruments (λ_{max} [nm] (ε)). Mass spectra (MS.) in electron ionization mode, CEC 21-490 *Bell-Howell* or HP 5980 GC-MS *Hewlett Packard* spectrometer (*m/z* [amu] (% base peak)). ^{1}H-NMR. spectra, *Varian* A 60A (60 MHz) or *Bruker* WP 80 CW (80 MHz) spectrometers: δ [ppm], apparent coupling constant *J* [Hz], number of protons, tentative attribution [LIS: relative shift induced by addition of Eu(fod)$_3$ or Eu(dpm)$_3$]. ^{13}C-NMR. spectra, *Bruker* WP 60 spectrometer (15.08 MHz, spectrum width: 3750 Hz, 4096 points, FT-Mode, deuterium signal of $CDCl_3$ as lock signal, δ_C of $CDCl_3$ as internal reference (76.91 ppm)): δ [ppm], apparent $^1J_{CH}$ coupling constant (± 1 Hz), tentative attribution; *s* singlet, *d* doublet, *t* triplet, *qa* quadruplet, *m* multiplet, 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), $CDCl_3$ as internal reference. Eu(fod)$_3$ and Eu(dpm)$_3$ from *Willow Brook Labs* (Waukesha, Wis., USA) were used without purification; vapour phase chromatography (GC.) and integrator, see [23]. Rotation angles $[\alpha]^{25}$, *Perkin Elmer* 141 polarimeter. Abbreviations: aq. aqueous, RT. room temperature, sat. saturated, sh. shoulder, THF tetrahydrofuran, *i.V. in vacuo*, BsCl *p*-bromobenzenesulfonyl chloride. Elementary analysis were performed by the microanalytical laboratory of the University of Geneva (Dr. *K. Eder*).

5,6-Dimethylidene-2-norbornanone (**7**). CrO_3 (22 g, 0.22 mol) was added under N_2 and portionwise to a solution of dry pyridine (34.8 g, 0.44 mol) in dry CH_2Cl_2 (500 ml) cooled to 0°. After stirring at RT. for 10 min, 5,6-dimethylidene-2*exo*-norbornanol (**14** [18]) (5 g, 0.0367 mol) in CH_2Cl_2 (20 ml) was added. After stirring at RT. for 1 h, the mixture was filtered through silica gel (200 g). The SiO_2 + residue was washed with CH_2Cl_2 (3 × 100 ml). Solvent was removed by distillation under reflux. The residue was distilled *i.V.*, a colourless liquid was obtained, 3.5 g (75%), b.p. 45°/1 Torr, *cf.* [18] [19].

*5,6-Dimethylidene-2*endo-*norbornanol* (**15**). Dry methanol (3.54 ml, 0.0876 mol) was added dropwise under N_2 to a stirred 1.39M solution of $LiAlH_4$ in dry THF. (20 ml) cooled to 0°. After 10 min at 0°, the ketone **7** was added (2.4 g, 0.0179 mol, in 6 ml THF) followed, after 1 h at RT., by 3 ml of aq. KOH 3N added dropwise with vigorous stirring at 0°. The precipitate was filtered off and the solution dried ($MgSO_4$). After removal of the solvent by distillation under reflux, the residue was distilled *i.V.* (b.p. 60°/0.01 Torr) and crystallized from pentane at −15°. Yield: 2.07 g (85%), white crystals, m.p. 34–35°. – UV. (isooctane): 254 (sh., 6100), 244.5 (9300), 239 (sh., 8000). – UV. (MeOH): 254 (sh., 5300), 245 (8050), 240 (sh., 7550). – IR. (CH_2Cl_2): 3560, 3090, 2970, 2890, 1640, 1395, 1120, 1045, 885. – ^{1}H- and ^{13}C-NMR.: *cf.* [19]. – MS. (70 eV): 137 (3), 136 (18), 118 (15), 117 (25), 107 (24), 105 (10), 103 (9), 94 (34), 93 (25), 92 (100), 91 (93), 79 (29), 78 (5), 77 (16), 65 (10).

$C_9H_{12}O$ (136.20) Calc. C 79.37 H 8.88% Found C 79.50 H 8.78%

exo-*5,6-Dimethylidene-2-norbornyl brosylate* (**11**). A solution of BsCl (8 g, 0.031 mol) in dry pyridine (10 ml) was added dropwise and under N_2 to a solution of alcohol **14** [18] (2.8 g, 0.021 mol) in dry pyridine (10 ml) cooled to 0°. After 15 h at 0°, the reaction mixture was poured into ice/water (100 g) under vigorous stirring. After extraction with ether (3 × 50 ml), drying ($MgSO_4$) and solvent removal *i.V.*, the crude brosylate **11** was dissolved in a minimum of boiling hexane, heated with active charcoal (0.2–0.5 g) and allowed to crystallize at 0°. Yield: 6 g (82%), white solid, m.p. 59–60°. – UV. (EtOH 96%): 234 (24,000). – IR. (KBr): 3100, 3000, 2960, 1580, 1340, 1190, 960. – ^{1}H-NMR. ($CDCl_3$): 7.78 (*m*, 4 H, arom.); 5.37, 5.10, 5.0 and 4.8 (br. *s*, 4 H, olefinic); 4.62 (*m*, 1 H, H–C(2)); 3.0 (*m*, 1 H, $^3J_{H-C(1),H-C(2)} \simeq 0$, H–C(1)); 2.85 (*m*, 1 H, $^3J_{H-C(4),H-C(3)} \simeq 3$ Hz, H–C(4)); 1.9–1.25 (*m*, 4 H, H_2C(3,7)). – ^{13}C-NMR. *cf.* [19]. – MS. (70 eV): 356 (3), 354 (3), 221 (4), 219 (4), 157 (13), 155 (13), 119 (54), 118 (100), 117 (25), 107 (17), 105 (13), 93 (26), 92 (17), 91 (100), 79 (13), 77 (14), 76 (10), 75 (9), 65 (11).

$C_{15}H_{15}BrO_3S$ (355.25) Calc. C 50.72 H 4.26% Found C 50.59 H 4.75%

endo-*5,6-Dimethylidene-2-norbornyl brosylate* (**12**). A solution of BsCl (4.3 g, 0.017 mol) in dry pyridine (10 ml) was added dropwise under N_2 to a solution of the *endo*-alcohol **15** (1.5 g, 0.011 mol) in dry pyridine (5 ml). After 15 h at 0°, the reaction mixture was poured into ice/water (100 g) under vigorous stirring. The crude brosylate **12** was filtered off and washed with cold water. After drying *i.V.* over P_4O_{10} and recrystallization from hexane, a white solid was obtained. Yield: 3.4 g (87%),

m.p. 87–88°. – UV. (EtOH 96%): 235.5 (25,000). – IR. (KBr): 3100, 3000, 2980, 1580, 1365, 1185, 960. – ^{1}H-NMR. ($CDCl_3$): 7.78 (*m*, 4 H, arom.); 5.4, 5.16, 4.91 and 4.9 (4 br. *s*, 4 H, olefinic); 5.4–4.9 (*m*, $^3J_{H-C(1),H-C(2)} \simeq 4$ Hz, H–C(2)); 3.05 (*m*, $^3J_{H,H} \simeq 4$ Hz, H–C(1)); 2.77 (*m*, $^3J_{H,H} \simeq 4$ Hz, H–C(4)); 2.15 (*m*, 1 H, $^3J_{H,H} = 13$, 10 and 4.5 Hz, H*exo*–C(3)); 1.6–1.1 (*m*, 3 H, H*endo*–C(3) and $H_2C(7)$). – ^{13}C-NMR. *cf.* [19]. – MS. (70 eV): 356 (17), 354 (17), 221 (9), 219 (9), 157 (23), 155 (23), 119 (33), 118 (100), 117 (81), 107 (26), 105 (20), 93 (46), 92 (25), 91 (100), 79 (15), 77 (16), 76 (15), 75 (14), 65 (14).

$C_{15}H_{15}BrO_3S$ (355.25) Calc. C 50.72 H 4.26% Found C 50.68 H 4.65%

exo-*5,6-Dimethylidene-2-norbornyl acetate* (**16**). A mixture of alcohol **14** (0.5 g, 3.6 mmol), dry pyridine (2 ml, 25 mmol) and acetic anhydride (1.8 ml) was stirred at RT. for 15 h under N_2. The reaction mixture was poured into ice/water (20 g) and extracted with ether (3 × 10 ml). The etheral extract was washed successively with aq. HCl-solution (10%, 3 × 10 ml) and aq. sat. $NaHCO_3$-solution (3 × 10 ml). After drying ($MgSO_4$), the solvent was removed by distillation under reflux. The residue was distilled *i.V.* Yield: 0.6 g (91.7%), colourless liquid with strong odour, b.p. 65%/0.5 Torr. – UV. (isooctane): 253 (sh., 6050), 244 (9450), 238 (sh., 8700). – UV. (MeOH): 253 (sh., 6050), 244 (9200), 238 (sh., 8000). – IR. (CH_2Cl_2): 3090, 2890, 1740, 1375, 1230, 1030, 885. – ^{1}H-NMR. ($CDCl_3$): 5.35, 5.15, 5.07 and 4.81 (4 br. *s*, 4 H, olefinic); 4.77 (*m*, 1 H, H–C(2)); 2.96 (*m*, 1 H, H–C(1)); 2.87 (*m*, 1 H, $^3J_{H,H} \simeq 4$ Hz, H–C(4)); 2.05 (*s*, 3 H, CH_3CO); 1.92 (*m*, 1 H, H*endo*–C(3)); 1.75 (*m*, 1 H, H*syn*–C(7)); 1.61 (*m*, 1 H, H*exo*–C(3)); 1.47 (*m*, 1 H, H*anti*–C(7)). – ^{13}C-NMR. *cf.* [19]. – MS. (70 eV): 178 (41), 149 (14), 136 (29), 135 (48), 134 (31), 118 (57), 117 (23), 107 (34), 93 (64), 92 (43), 91 (100), 79 (13), 77 (10), 65 (12).

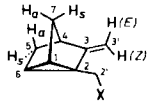
$C_{11}H_{14}O_2$ (178.24) Calc. C 74.12 H 7.92% Found C 74.04 H 7.96%

endo-*5,6-Dimethylidene-2-norbornyl acetate* (**17**). Same procedure as described for the acetate **16**, using the alcohol **15** (0.5 g, 3.6 mmol). Yield: 0.58 g (89%), colourless liquid, b.p. 65°/0.5 Torr. – UV. (isooctane): 253 (sh., 5750), 243.5 (8750), 239 (sh., 8000). – UV. (MeOH): 253 (sh., 5600), 244 (8500), 239 (sh., 7900). – IR. (CH_2Cl_2): 3080, 2960, 2880, 1730, 1375, 1300, 1225, 1135, 1120, 885. – ^{1}H-NMR. ($CDCl_3$): 5.37, 5.24, 4.91 and 4.90 (4 br. *s*, 4 H, olefinic); 5.09 (*m*, 1 H, H*exo*–C(2)); 3.21 (*m*, 1 H, $^3J_{H,H} \simeq 4$ Hz, H–C(1)); 2.84 (*m*, 1 H, $^3J_{H,H} \simeq 4$ Hz, H–C(4)); 2.25 (*m*, 1 H, H*endo*–C(3)); 2.01 (*s*, 3 H, CH_3CO); 1.78–1.12 (*m*, 3 H, H*exo*–C(3) and $H_2C(7)$). – ^{13}C-NMR., *cf.* [19]. – MS. (70 eV): 178 (91), 148 (18), 135 (44), 134 (75), 133 (44), 119 (15), 118 (100), 117 (32), 107 (42), 94 (28), 93 (81), 92 (49), 91 (91).

$C_{11}H_{14}O_2$ (178.24) Calc. C 74.12 H 7.92% Found C 74.29 H 7.88%

Buffered acetolysis of **11** (and **24**). Acetic acid, AcOK were prepared as before [23]. The brosylate **11** (or **24**) (2 g, 5.6 mmol) and a solution of AcOK 0.6M in AcOH (12 ml) containing 1% *(v/v)* of acetic anhydride were placed in a Pyrex tube (25 ml) that was sealed *i.V.* after complete degassing *i.V.* After 3 days at 25° (*ca.* 15 $\tau_{1/2}$), the Pyrex ampoule was frozen in liq. N_2, opened under N_2, poured into ice/water (10 g), and extracted with ether (3 × 15 ml). The organic extract was washed successively with H_2O (3 × 20 ml) and with a sat. aq. $NaHCO_3$-solution (3 × 20 ml). After drying ($MgSO_4$), the solvent was removed by distillation under reflux. Analytical GC. (Ucon HB 5100, 10% on WAW 80/100 chromosorb, 2.4 × 4 mm Pyrex column, 130°, 30 ml/min He) showed two acetates **16**/**18** (or **26**+**27**/**28**) in the ratio 25/75 and < 1% of 5,6-dimethylidene-2-norbornene identified by coinjection of **4** (X = CH_2) prepared independently [51] (tetradecane as internal standard). The residue was distilled *i.V.* Yield: 0.983 g (98%), colourless liquid, b.p. 64–67°/0.5 Torr, consisting of **16** and **18**. These were separated by preparative GC. (Ucon LB 1800 X, 20% on WAW 60/80 mesh chromosorb, 3.2 m × 8 mm Pyrex column, 130°, 160 ml/min H_2). The first fraction **18**, the second fraction **16**, identified by comparison with **16** prepared independently, see above.

(3-Methylidene-2-nortricyclyl)methyl acetate (**18**). – UV. (isooctane): 216 (250). – IR. (CH_2Cl_2): 3070, 3000, 2950, 2870, 1730, 1685, 1375, 1230, 1025, 875. – ^{1}H-NMR. (C_6F_6, 30° [LIS: Eu(fod)$_3$]): 4.32 (*s*, 2 H, H_2C–OAc [97%]); 4.22 (*s*, 1 H, H(*Z*) olefinic [33%]); 4.05 (*s*, 1 H, H(*E*) olefinic [24%]); 2.26 (*m*, H–C(4) [14%]); 2.03 (*s*, 3 H, CH_3CO [100%]); 1.62 (*s*, 2 H, H–C(1,6) [31%]); 1.59 (*d*, 10 Hz,



18 X = OAc
19 X = OH

2 H, H*syn*–C(5,7) [16%]); 1.36 (*d*, 10 Hz, 2 H, H*anti*–C(5,7) [6.5%]). – ^{13}C-NMR. ($CDCl_3$): 170.5 (*m*, CO), 154.7 (br. *s*, C(3)); 97.2 (*t*, $^1J_{C,H}$ = 157.5 Hz, $H_2C(3')$); 61.4 (*t*, 147.5, $H_2C(2')$–OAc); 33.6 (*d*, 143, C(4)); 32.4 (*t*, 136, C(5,7)); 25.8 (*s*, C(2)); 20.8 (*qa*, 129.5, CH_3); 20.3 (*d*, 175, C(1,6)). – MS. (70 eV): 178 (24), 149 (16), 136 (45), 135 (65), 134 (40), 118 (100), 117 (100), 108 (45), 93 (69), 92 (43), 91 (100).

$C_{11}H_{14}O_2$ (178.24) Calc. C 74.12 H 7.92% Found C 74.24 H 7.97%

The products of acetolysis **16** and **18** could also be separated by TLC. on SiO_2 + 10% $AgNO_3$ (hexane/AcOEt 15:85).

Buffered acetolysis of **12** (and **25**). Same procedure as above, 4 days at 100°. Yield: 94% of a 90:10 mixture of **16**/**18** (or **29** + **30**/**31**) separated by GC. (same conditions as above).

(3-Methylidene-2-nortricyclyl)methanol (**19**). A solution of acetate **18** (0.7 g, 3.9 mmol) in dry THF (2 ml) was added dropwise under N_2 to a stirred suspension of $LiAlH_4$ (0.17 g, 4.5 mmol) in THF (3 ml) maintained at 0°. After stirring for 1 h at RT., aq. KOH 3N (0.3 ml) was added. The precipitate was filtered off, washed with ether (2 × 10 ml) and the solution dried ($MgSO_4$). The solvent was removed by distillation under reflux, the residue distilled *i.V.* Yield: 0.52 g (97%), colourless liquid, b.p. 60°/0.05 Torr. – UV. (isooctane): 218.5 (200). – IR. (CH_2Cl_2): 3630, 3480, 3070, 3010, 2950, 2880, 1685, 1410, 1170, 1015, 990, 875. – ^{1}H-NMR. ($CHCl_3$ 25° [LIS: Eu(dpm)$_3$]): 4.75 (*s*, 1 H, H(Z) olefinic [40%]); 4.62 (*s*, H(E) olefinic [33%]); 3.85 (*s*, 2 H, $H_2C(2')$–OH [100%]); 2.25 (*m*, H–C(4) [20%]); 1.57 (br. *s*, 2 H, H–C(1,6) [35%]); 1.56 (br. *d*, 10 Hz, 2 H, H*syn*–C(5,7) [23%]); 1.36 (br. *d*, 10 Hz, 2 H, H*anti*–C(5,7) [6%]). – ^{13}C-NMR. ($CDCl_3$): 155.6 (br. *s*, C(3)); 97.1 (*t*, 156.5, H_2C=C(3)); 59.7 (*t* × *t*, $^1J_{C,H}$ = 142, $^3J_{C,H} \simeq 2$, $H_2C(2')$–OH); 37.7 (*d*, 150, C(4)); 33.9 (*t* × *m*, 132.5, C(5,7)); 28.9 (*m*, C(2)); 20.4 (*d*, 177, C(1,6)). – MS. (70 eV): 136 (18), 117 (19), 107 (27), 105 (24), 94 (31), 93 (21), 92 (100), 91 (35), 79 (33).

$C_9H_{12}O$ (136.2) Calc. C 79.37 H 8.88% Found C 79.29 H 8.89%

Titrimetric rate constants of the buffered acetolysis of **11**. Standard solution of AcOK 0.125M in AcOH + 1% *(v/v)* Ac_2O was titrated with $HClO_4$ 0.1N in AcOH *(Merck)* using 'Crystal Violet' as indicator. 1.5 to 2.5 · 10^{-3}M solution of AcOK were prepared by dilution with AcOH + 1% Ac_2O of the above standard solution.

The *exo*-brosylate **11** (7.5 mg, 0.021 mmol) was dissolved under dry N_2 in 10 ml of a 2.5 · 10^{-3}M solution of AcOK in AcOH + 1% *(v/v)* Ac_2O (1.18 mol-equiv. of AcOK). This solution was transferred under dry N_2 into 1 cm quartz cells and the acetolyses were followed by UV. absorption spectroscopy (*Pye Unicam* SP8-100). The difference of absorbance at 276.5 and 300 nm was recorded as function of time [30] (automatic recording of data on floppy disc, 4 cells simultaneously with automatic cell interchange). Least square regressions were made directly on the exponential laws [52] (computer, adapted LSKIN 1 program [53]). The first order rate constants were found from 6–10 independent measurements at the same temperature. Thermostatization, thermostat *Haake* (±0.02°) with high flow pump. Temperature reading, directly in the cells by a Pt-resistance (Pt-100) that was standardized against a quartz thermometer (*Hewlett Packard* 2804 A). Temperature stabilization inside the cells: better than ±0.05°.

Salt effects on the buffered acetolysis of **11**. Standard solutions of LiOAc were prepared by dissolving weighed amounts of Li_2CO_3 in AcOH + 1% *(v/v)* Ac_2O. Idem for standard solutions of $LiClO_4$ and KOBs.

Li_2CO_3 *(Merck, p.a.)* and $LiClO_4$ *(Fluka, p.a.)* were dried under atmospheric pressure at 180° for 4 days and stored in a dessicator. Potassium *p*-bromobenzenesulfonate (KOBs) was obtained by hydrolysis of BsCl (48 h, under reflux) and neutralization with KOH. The crude KOBs was recrystallized from water until negative chloride ion test ($AgNO_3$).

$C_6H_4BrO_3SK$ (275.16) Calc. C 26.19 H 1.47 Br 29.04% Found C 26.28 H 1.70 Br 29.26%

exo-*5,6-Dimethylidene-2-norbornyl*-p-*toluenesulfonate* (**21**). Potassium *p*-toluenesulfonate (KOTs) was prepared by heating TsOH · H_2O (1 g, 5.3 mmol) and Ac_2O (0.537 g, 5.3 mmol) in 40 ml AcOH + 1% *(v/v)* Ac_2O to 100° for 1 h under N_2. After cooling to RT., anhydrous K_2CO_3 (1.1 g, 8 mmol) was added and the solution was stirred for 1 h at 35°. The *exo*-brosylate **11** (0.5 g, 1.4 mmol) was then added, and after 1 h (*ca.* 1 $\tau_{1/2}$) at 35°, the mixture was poured into ice/water (50 g) and extracted with ether (3 × 20 ml). The ethereal extract was washed with water (3 × 20 ml), then with

sat. aq. $NaHCO_3$-solution (3×20 ml). After drying ($MgSO_4$), the solvent and the volatile acetates **16**+**18** were distilled off *i.V.* The residue consisted of **21** (*ca.* 15%) and **11** (*ca.* 35%) (^{1}H-NMR., see text). Compound **21** was also obtained by esterification of the *exo*-alcohol **14** with TsCl (1 mol-equiv.) in pyridine at 0° for 15 h, and usual work-up.

Titrimetric rate constants of the buffered acetolysis of **12**. The *endo*-brosylate **12** (*e.g.:* 37.5 mg) was dissolved under N_2 in 50 ml $2.5 \cdot 10^{-3}$M AcOK in AcOH+1% *(v/v)* Ac_2O (0.0021M in **12**). Aliquots of 2.3 ml of this solution were transferred (syringe) into 5 ml Pyrex ampoules (treated with $K_2Cr_2O_7+H_2SO_4$, then successively with H_2O, EtOH, CH_2Cl_2, dried to 180°, cooled to RT. under dry N_2) which were sealed under atmospheric pressure of dry N_2 and immersed in a thermostated oil bath (±0.05°). After various periods of time, the ampoules were frozen in liq. N_2. After warming to RT., the ampoules were opened and transferred into a 1 cm quartz cell under N_2. The absorbance at 300 and 276.5 nm was measured and the difference analyzed as above.

Polarimetric rate constants of the buffered acetolysis of (+)-**11**. The *exo*-brosylate (+)-**11** [35] (4.2 mg) was dissolved in 1.1 ml of 0.125M AcOK in AcOH+1% *(v/v)* Ac_2O (0.107M in (+)-**11**). This solution was transferred under N_2 into the cylindrical cell (length: 10 cm) of the polarimeter thermostated at 25.0±0.1°. The rotation angle $[\alpha]_{365}^{25}$ was measured as a function of time. The data treated by computer [53] allowed calculation of the first order, polarimetric rate constant ($k_{\alpha\,(exo)}$ from 4 independent measurements; *Table 3*). The final solution of 4 kinetics measurements were combined and poured into ice/water. The volatile acetates **16**+**18** were extracted and purified as above. This mixture gave $[\alpha]_{365}^{25} = \pm 0.002$.

Polarimetric rate constant of the buffered acetolysis of (+)-**12**. The ampoule technique described above for the acetolysis of **12** was applied to the acetolysis of a 0.021M solution of (+)-**12** and 0.025M AcOK in AcOH+1% *(v/v)* Ac_2O. The $[\alpha]_{365}^{25}$ of aliquots (22–30) of 1.1 ml allowed evaluation of $k_{\alpha\,(endo)}$ at 121±0.05° (3 independent measurements at the same temperature; *Table 3*).

exo-*3*exo-*Deuterio-5,6-dimethylidene-2-norbornyl brosylate* (**24**). A solution of freshly distilled BF_3 etherate (12 g, 0.082 mol) was added dropwise under N_2 to a vigorously stirred suspension of $NaBD_4$ (*Fluka,* 2.6 g, 0.069 mol) and *trans*-5,6-bis(chloromethyl)-2-norbornene (10 g, 0.052 mol) [51] in dry THF (30 ml) cooled to 0°. After stirring for 3 h at RT., the mixture was cooled to 0° and aq. KOH 3N (15 ml) was added dropwise, followed by H_2O_2 30% (12 ml, 0.118 mol). After stirring for 24 h at RT., the mixture was extracted with ether (5×10 ml). The ethereal extract was dried ($MgSO_4$) and evaporated to dryness. The residue was distilled *i.V.* Yield: 8.6 g (79%), colourless oil, b.p. 100°/0.01 Torr. – ^{1}H-NMR. ($CDCl_3$): 4.05 (*m*, 1 H); 4.0–3.0 (*m*, 4 H); 2.5–1.0 (*m*, 7 H).

This mixture of (*3exo*-D)-5,6-bis(chloromethyl)-*2exo*-norbornanols (5 g, 0.024 mol) was heated under reflux and N_2 with KOH (4.0 g, 0.071 mol) in abs. ethanol (15 mol) for 3 days. After cooling to RT., water was added (30 ml) and the mixture was extracted with CH_2Cl_2 (5×20 ml). The organic extract was washed with water (2×50 ml) and dried ($MgSO_4$). The solvent was evaporated and the residue distilled *i.V.* Yield: 2.5 g (76%), colourless liquid, b.p. 50°/0.01 Torr. Spectral data were consistent with (*3exo*-D)-5,6-dimethylidene-*exo*-2-norbornanol (*cf.* **14** [18] [19]). – ^{1}H-NMR. ($CDCl_3$): 5.34, 5.20, 5.04 and 4.90 (4 br. *s*, 4 H, olefinic); 4.0 (*m*, 1 H, H–C(2)); 2.85 (*m*, 2 H); 2.2–1.3 (*m*, 3 H). – MS. (70 eV): 98–99% D_1.

Brosylation of this alcohol (2.5 g, 0.0184 mol) with BsCl/pyridine as described for the preparation of **11**, yielded 5.2 g (80%) of **24**, white powder, m.p. 59–60°. – IR. (KBr): 3100, 2990, 2960, 2890, 1580, 1370, 1190, 1170. – ^{1}H-NMR. ($CDCl_3$): 7.78 (*m*, 4 H, arom.); 5.37, 5.10, 5.00 and 4.80 (4 br. *s*, 4 H, olefinic); 4.62 (*d*×*m*, 7 Hz, H–C(2)); 3.0 and 2.85 (*m*, 2 H, H–C(1,4)); 1.8 (*m*, H*endo*–C(3)); 1.76 and 1.46 (*m*, H_2–C(7)), see *Figure 1*. – ^{2}H-{^{1}H}-NMR. ($CDCl_3$): 2.03 ppm, see *Figure 2*.

endo-*(2*exo-*D)-5,6-Dimethylidene-2-norbornyl brosylate* (**25**). Dry MeOH (1.9 ml, 47 mmol) was added dropwise under N_2 to a stirred 1.39M solution (11.4 ml) of $LiAlD_4$ *(Fluka)* in dry THF cooled to 0°. After 10 min at 0°, the ketone **7** (1.3 g, 9.7 mmol) in 3.5 ml dry THF was added dropwise. After stirring at RT. for 1 h, the mixture was cooled to 0° and aq. KOH 3N (1.6 ml) was added dropwise. The precipitate was filtered off and the solution dried ($MgSO_4$). After evaporation of the solvent under reflux, the residue was distilled *i.V.* Yield: 1.2 g (90%) of (*2exo*-D)-5,6-dimethylidene-*2endo*-norbornanol. – ^{1}H-NMR. ($CDCl_3$): 5.5, 5.2, 5.0 and 4.9 (4 br. *s*, 4 H, olefinic); 2.9 and 2.75 (*m*, H–C(1,4)); 2.2, 1.6, 1.45 and 1.0 (*m*, 4 H, H_2–C(3,7)).

Brosylation of this alcohol (1 g, 7.3 mmol) with BsCl/pyridine, as described above for the preparation of **12**, yielded 2.3 g (90%) of **25**. – IR. (KBr): 3100, 3000, 2890, 1580, 1360, 1195, 950,

940. – ^{1}H-NMR. ($CDCl_3$): 7.78 (*m*, 4 H, arom.); 5.4, 5.16, 4.91 and 4.9 (4 br. *s*, 4 H, olefinic); 3.05 (*m*, H–C(1)); 2.77 (*m*, H–C(4)); 2.15 and 1.3 (*d*×*d*, $H_2C(7)$); 1.5 (*m*, $H_2C(3)$); *cf. Figure 3.* – ^{2}H-{^{1}H}-NMR. ($CDCl_3$ + CCl_4): 5.17 ppm, *cf. Figure 4.*

Deuteriated exo-*5,6-dimethyl-5-norbornen-2-yl acetates* **32**. The bicyclic acetates **26** + **27** or **29** + **30** (0.23 g, 1.29 mmol) in pentane (5 ml) were partially hydrogenated in presence of 5 mg of Pd/C 5% at 0°. When 1 mol-equiv. of H_2 was absorbed (28–30 ml), the reaction mixture was degassed *i.V.* and stirred in presence of the catalyst for 15–20 min at RT. After filtration and removal of the solvent under reflux, the crude **32** was purified by GC. (OV 225 20% on WAW 60/80 mesh Chromosorb). The deuterium analysis (see text) was made by MS. (EI, 70 eV, average of at least 20 spectra); IR. and NMR. data of **32** were similar to those reported for the unlabelled derivative [39].

Diels-Alder *adducts of methyl vinyl ketone to* **26** + **27** *and* **29** + **30** (**33**). The dienes **26** + **27** or **29** + **30** (0.1 g, 0.56 mmol), 0.3 g of freshly distilled methyl vinyl ketone and 5 mg hydroquinone were heated to 80° for 14 h in a Pyrex tube sealed *i.V.* After removal of the excess of methyl vinyl ketone *i.V.*, the mixture of adducts **33** was purified by TLC. (SiO_2, acetone/$CHCl_3$ 1:4). Yield: 0.11 g (80%), colourless oil, b.p. 80°/0.01 Torr. Deuterium analysis, MS. (EI, 70 eV, average of at least 20 spectra).

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