Solvolysis of some substituted benzonorbornenyl derivatives

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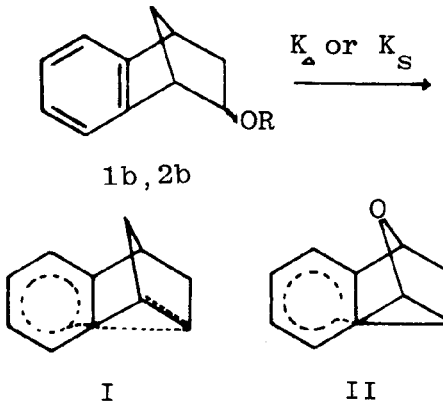
Summary: The epimeric alcohols **5a/7a** and **12a/14a** have been synthesized and the solvolysis of their p-toluenesulphonates has been investigated. A small accellaration in the rate ratio for the exo/endo epimers has been observed, explained on the basis of the cation IV. No steric effects have been observed due to the introduction of the methyl group as is evident in the solvolysis of **12a/14a** derivatives.

Introduction

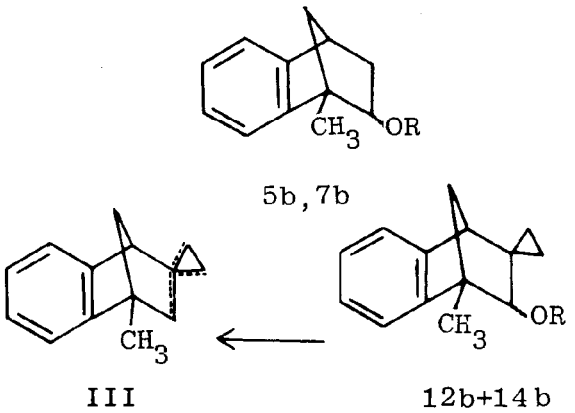
The structure of Benzonorbornen-2-yl cation formed in the solvolysis of 2-exo- and 2-endo-benzonorbornenyl derivatives **1 b** and **2 b** has been generally postulated to be of the type I [1,2], whereby the π -electrons of the aromatic nucleus overlap with the p-orbital formed at C-2 through the $C_1 - C_5$ bond. Such a species can result by the direct participation of the aromatic nucleus



in the bond breaking process (K_Δ -process) or is formed in the subsequent stages of the reaction from a 'classical' carbonium ion (K_s -process).

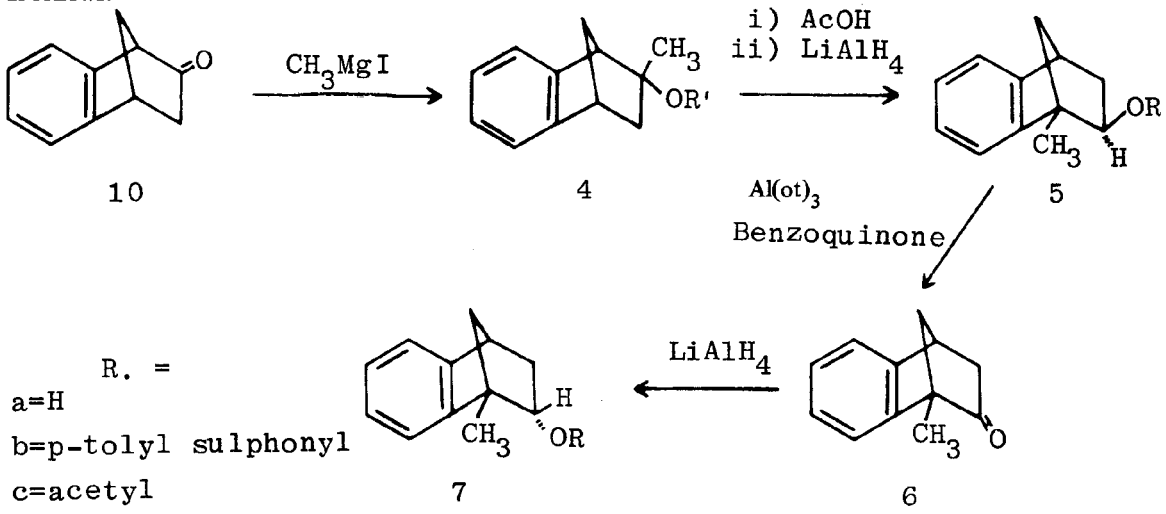
Pcquette et al[3] on the other hand, formulate yet another type of cation II, based on their studies of 9-oxo-benzonorbornen-2yl derivatives, thought to be formed by the direct overlap of the aromatic nucleus with the p-orbital at C-2. To determine which of the two structures is a more exact representation of the benzonorbornenyl cation, it was thought to introduce a stabilizing group like methyl group at C-1 which will stabilize a cation of the type I but would not show any significant effects for a cation of the type II.

Esters **5b** and **7b** were synthesized and their solvolysis studied. Moreover, to examine whether the introduction of the methyl group causes any steric changes in the system, 3-cyclopropyl substituted esters **12b** and **14b** were also synthesized and their solvolysis studied, because it is known that a neighbouring cyclopropyl group can effect a strong stabilization in cations like III, shielding it from any other neighbouring group effects [4] so that any extra stabilization found in the case of **12b** and **14b** could safely be attributed to the steric effects due to the methyl group.



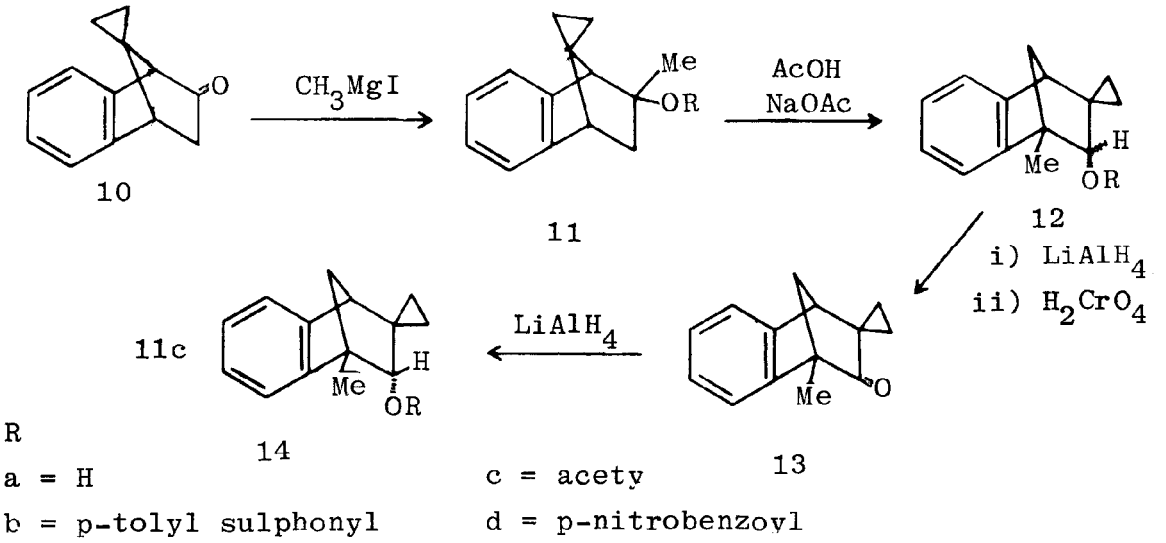
Synthesis.

The epimeric alcohols **5a** and **7a** were synthesized as follows:



The acid catalysed rearrangement of 2-exo-methyl-5.6-benzo-(5)-norbornen-2-endo-ol **4**[5]) obtaied by the Grignard reaction of benzonorbornen-2-one **3** with methyl-magnesium iodide gave 1-methyl-(5.6)-benzo-(5)-norbornen-2-exo-acetate **5c** in about 75% yield. Lithium aluminium-hydride reduction of this ester, obtained by preparative gas chromatography, produced the alcohol **5a**, which was oxidised by Oppenauer method using aluminium ter-butoxide and p-benzoquinone [6] to give the ketone 6. This again was reduced to the epimeric 2-**endo**-alcohol **7a** with lithium aluminiumhydride in ether.

The other epimeric pair of alcohols **12a** and **14a** was obtained by the following scheme:



The tertiary alcohol **11a**, obtained by the Grignard reaction of spiro- cyclopropane-1.7′ -(5′.6′)-benzo-(5′)-norbornen -2′ - one **10** with methyl magnesium iodide[7]) was converted into its p-nirobenzoate **11d**. Preparative solvolysis of this ester gave a mixture of acetates consisting of 3 components. After preparative gas chromatographic separation, one of these (22%) was identified as the acetate of the starting alcohol **11c**. The other two components were identified on the basis of their spectra as the isomeric acetates **12c** (67%) and **14c** (11%).

Reduction of the acetate **12c** with lithium aluminiumhydride gave the alcohol **12a** which was oxidised by the two phase oxidation method [8] to the ketone **13**, which was reduced by lithium aluminiumhydride in ether to the isomeric alcohol **14a**, identical to the hydrolysis product obtained from the acetate **14c**.

The alcohols **5a, 7a, 12a** and **14a** were converted into their corresponding tosylates **5b, 7b, 12b,** and **14b** by treatment with p-tolysulfonylchloride in pyridine at 0°C.

Results and Discussion

The 2-exo-ester **5b** solvolyses in 80% acetone at 100°C with a reaction rate of $5{,}4 \times 10^{-2}$ sec^{-1}, which is approximately eight times as fast as the unsubstituted derivative [1] whereas the 2-endo-ester **7b** solvolyses under the same conditions at a rate of $2{,}32 \times 10^{-6}$ $sec.^{-1}$, which is roughly twice the rate of the corresponding unsubstituted derivative [1,2] (table-1).

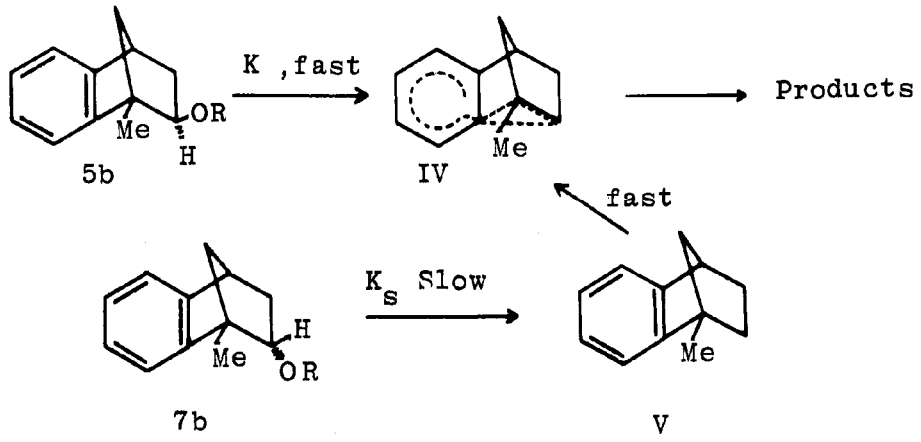
In compound which undergo solvolytic reactions without neighbouring group participation, introduction of a β -methyl group generally causes an increase in the rate of reaction to the order of 10^4; in the 2-norbornyl system, however,only a moderate increase in the **exo/endo** rate ratio of about 45 has been observed[9]. The small increase in the solvolysis of **5b** and **7b** can be explained on the basis of a carbonium ion IV analogous to the thpe I rather than by II in which there is no involvement of C-1.

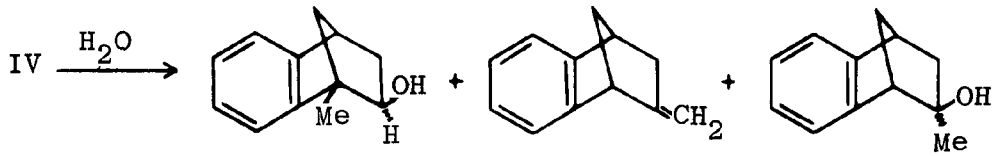
The geometry of the C-1, which is more tetragonal with only partial carbonium ion character rather than the trigonal which is necessary for resonance, appears to be the reason in the formation of the carbonium ion IV.

The reaction mixture obtained on solvolysis of **5b** contained besides 5% **5a** and about 10% of an olefinic fraction 8, purification as the **endo** isomer of **4** on the basis of its NMR-spectrum. The olefin 8 was identified similarly as 2-methylene- (5.6)-benzo-(5)-norbornene.

Similar products were isolated by the solvolysis of the 2-endo-ester **7b**; the product ratio was, however quite different. The mixture contained about 1% **5a**, 80% **8**, 12% **9a** and 6-7% unidentified material. The high ratio of olefin indicates that the alcohol **5a** and **9a** are probably unstable at the high temparature required for the preparative solvolysis.

In order to check, whether this small increase might result from the steric effects of the methyl group, the solvolysis of the esters **12b** and **14b** was studied. These





5a 8 9a

solvolyse in 80% acetone at 25°C with a rate constant of 8,76 x 10^{-5} sec^{-1} and 6,6 x 10^{-5} $sec.^{-1}$ respectively. These values are nearly identical to those observed for compounds without the methyl group (table 1). As the cyclopropyl cation can not be effected further by neighbouring groups [4a], any eventual increase in the reaction rates would have resulted from the steric accellaration from these groups. The observed results indicate that no such effects are present in the solvolysis of **12b** and **14b**.

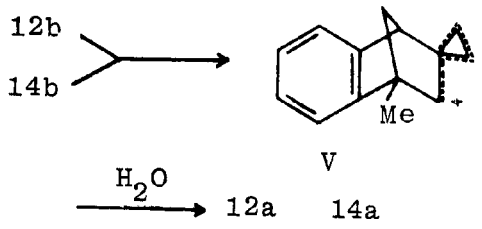
As the product of solvolysis from both **12b** and **14b** only non-rearranged alcohols **12a** and **14a** were isolated. Two other minor products, apparantly olefinic compounds, were not persued further. The **exo/endo** product ratio was found to be 2, smaller than the value of 7-9 found for the unsubstituted derivatives [4a]. The C-1 methyl group probably hinders the solvent at-

Table -1

Compound	Temp. °C	Rate constant Sec^{-1}	$\Delta H^{\ddagger}$ KC als.	$\Delta S^{\ddagger}$ esu	k_{exo}/k_{endo}
	25,0 [b,c]	3,28x 10^{-5}			
	32,6±0.05	8,20 ± 0,4 x 10^{-5}	21,3	-7,8	24000 at 100°C
5b	60,4 ± 0,05	1,65 ± 0,07 x 10^{-3}			
	100,0 *f)*	5,54 x 10^{-2}			
7b	100,0 ± 0,05 [b]	2,32 ± 0,2 x 10^{-6}			
	0,1 ± 0,05 [b]	2,32 ± 0,23 x 10^{-5}	23,3	-5,6	13,2 at 25°C
12b	25,0 ± 0,03	8,76 ± 0,03 x 10^{-4}			
	25,0 b,c)	6,60 x 10^{-5}			
14b	29,93 ± 0,03	1,25 ± 0,02 x 10^{-4}	22,7	11,4	
	50,0 ± 0,03	1,39 ± 0,01 x 10^{-3}			
	25,0 [b,d]	1,80 x 10^{-6}			
	100,0 [b,d]	6,71 x 10^{-3}	23,6	-5,8	5400 at 100°C
	100,15 [b,d]	1,23 ± 0.03 x 10^{-6}	25,0	3,5	
	25,0 [b,d]	6,76 ± 0,05 x 10^{-4}	22,2	1,5	12,2 at 25°C
	25,0 [b,d]	5,57 ± 0,03 x 10^{-5}	22,0	-4,3	

All measurements were done in 80% acetone-water. a) R = p-nitrobenzoate b) R = tosylate c) Calculated from values at other temparatures d) see ref. 4a.

tack from the favourable *exo*-side on the cation IV. In analogy to the previous work [4a] the mechanism can be written as:



Experimental

1-methyl-(5.6)-benzo-(5)-norbornen-2'-exo-ol **5a**

5,0 g (29 mmol) 2-*exo*-methyl-(5.6)-benzo-(5)-norbornen-2-*endo*-ol 4[5]) were placed in 50 ml of glacial acetic acid and after the addition of 5 ml of conc. H_2SO_4 were refluxed for 40 h. After cooling to room temparature, the reaction mixture was poured in 200 ml of ice water and extracted repeatedly with ether; the ether phase was washed with $NaHCO_3$ solution, dried over Na_2SO_4 and the solvent removed. The major component of the acetate mixture (75%) was isolated by preparative gas chromatography (5m UCON-CB-500 on Chromosorb-G). 500 mg of this acetate **5c** were reduced with 60 mg (ca. 1,5 mmol) of lithium aluminiumhydride in 10 ml dry ether and worked up as usual. Bulb to bulb distillation of the product gave **5a** in 90% yield, m.p 111-112°C from pentane.

$C_{12}H_{14}O$ (174,2) requires C 82,72; H 8,10; found C 82,63 H 8,25.

IR-Spectrum (KBr) : 3310, 1460, 1290 and 1040 cm^{-1}. NMR-Spectrum ($CDCl_3$) ; τ=2,78-2,97 (m,4H); 6,28-6,50 (m, 1H, C-2); 6,72-6,88 (m. 1H, C-4); 7,77 (s, 1H, -OH); 7,87-8,40 (m, 4H); 8,48 (s, 3H).

1-methyl-(5.6)-benzo-(5)-norbornen-2-exo-p-toluenesulfonate **5b**

100 mg (ca.0,6 mmol) **5a** were treated with 140 mg (ca. 0.75 mmol) p-toluene sulfonylchloride in pridine to give 150 mg (ca. 76% yield) **5b**, m.p. 83-85°C (decomp.) from pentane. $C_{19}H_{20}O_3S$ requires C 69,50; H 6,14; S 9,74; found C 69,77; H 6,06; S 9,69.

IR-Spectrum (KBr): 1460, 1350, 1330, 1180 and 1050 cm^{-1}. NMR-Spectrum ($CDCl_3$): τ = 2,06-2,78 (q, J=28,0 Hz., J' =8,0 Hz., 4H); 2,78-2,98 (m, 4H); 5,57-5,70 (m, 1H); 7,53 (s, 3H); 7,80-8,38 (m, 4H); 8,52 (s, 3H).

1-methyl-(5.6)-benzo-(5)-norbornene-2-endo-ol **7a**

200 mg (ca. 1,2 mmol) 1-methyl-(5,6)-benzo-(5)-norbornen-2- one **6** [5]) were reduced with 20 mg (ca. 0.5 mmol) lithium aluminiumhydride in 20 ml dry ether and worked up as usual. Distillation at 10 torr and bath temparature of 120-140°C gave 180 mg (ca. 90% yield) **7a**, m.p. 51-53°C from pentan. $C_{12}H_{14}O$ (174,2) requires C 82,72, H 8,10; found C 82,69 H 8,32.

IR-Spectrum (KBr) : 3320, 1470, 1290, 1040 cm^{-1} NMR-Spectrum ($CDCl_3$) : τ = 2,83-3-00 (m, 4H); 5,80-6,07 (m, 1H, C-2); 6,72-690 (m, 1H, C-4); 7,20-8,37 (m, 3H); 8,53 (s, 3H); 8,95-9,65 (m, 2H).

1-methyl-(5-6)-benzo-(5)-norbornen-2-endo-p-toluenesulfonate **7b**.

150 mg (ca. 0,9 mmol) **7a** were treated with 220 mg (1,2 mmol) p-toluene sulfonylchloride as above to give 150 mg (70% yield) **7b**, m.p. 135-137°C from pentane. $C_{19}H_{20}O_3S$ requires C 69,50; H6,14; S 9,74 found C 69,74; H 5,86 S 9,75.

Table - 2 : Product distribution in the solvolysis of the esters **5b**, **7b**, **12b**, and **14b**

Compound	12a	14a	8	5a	9a	unknown
12b	55,1%	28,0%	–	–	–	16,9%
14b	55,6%	32,3%	–	–	–	12,1%
5b	–	–	9,8%	5,3%	84,1%	0,8%
7b	–	–	80,0%	1,0%	12,0%	7,0%

IR-Spectrum (KBr): 1350, 1180, 1100, 1010 cm^{-1}. NMR-Spectrum ($CDCl_3$) : τ = 2,18-2,90 (m, 8H); 4,90-5,17 (dd, J=9,0 Hz., 1H); 6,70-6,88 (m, 1H); 7,40-7,90 (m, 4H) 8,25 (s, 3H); 8,63-9,02 (m, 1H).

Preparative solvolysis of **5b** and **7b**

100 mg (ca. 0,3 mmol) tosylates **5b** and **7b** respectively were dissolved in 10 ml of 80% acetone with 50 mg 2,6-lutidine and heated under reflux for atleast 10 half life times for the reaction. After cooling to room temparature, most of the acetone was removed under low vacuum at room temparature and the reaction product taken up in ether. The ethereal solution was washed repeatedly with cold dil. H_2SO_4, followed by sodium bicarboated solution, dried over $MgSO_4$ and ether removed under vacuum. The crude product (about 40 mg) was examined by g.l.c. (see table-2) and the two major products were isolated by preparative g.l.c. The olefinic component (m/e = 156 ; $C_{12}H_{12}$) gave an NMR-Spectrum (CCl_4) consisting of multipletts at τ = 2,86-3,15 (4H) ; 5,00-5,08 (1H0; 6,30-6,67 (2H, C-1 and C-4); 7,40-8,40 (broad m, 4H) consistent with the proposed structure **8**.

The second component, m.p. 88-89°C from petrol ether 40-60°C p-nitrobenzoate mp.p 112-113°C was identified as **9a** (lit. [9] m.p. 88,6-89,5°C; p-nitrobenzoate m.p. 112-114°C). In $CDCl_3$ there were multiplets at τ = 2,89-3,10 (4H); 6,62-6,87 and 7,00-7,15 (2H, C-1 and C-4); 7,55-8,30 (4H); 8;85 (1H) and a singlet at 9,05 for the methyl protons.

Spiro- cyclopropane-1.7' - 2' -exo-methyl-(5'.6') -benzo-(5')-norbornen-2'-endo-ol **11a**

To solution prepared from 27,0 g (0,19 mol) methyl iodide and 5,1 g (0,19 g atom) magnesium in 100 ml dry ether were added 32,0 g (174 mmol) spirocydlopropane-1.7' - (5'.6')-benzo-(5')-norbornen-2'-one **10** in 100 ml dry ether dropwise with stirring. After 4 hrs., the mixture was hydrolysed wih a moderatly concentrated NH_4Cl solution and the aqeous phase extracted thrice with ether. The combined ether fractions were then worked up as usual. Recrystallisation from pentane gave 25,4 g (73%) **11a** m.p. 79-80°C. $C_{14}H_{16}O$ (200,3) requires C 83,94, H 8,04; found C 83,77, H 8,17.

IR-Spectrum (KBr): 3460, 1460, 1370, 1230 and 1180 cm^{-1} NMR-Spectrum (CCl_4) : τ =2,75-3,08 (m, 4H); 7,50-8,06 (m, 3H); 8,43 (s, 3H); 8,63-8,90 (m, 1H); 9,15-9,66 (m, 4H).

Spiro-cycolpropane-1.7'-2'-exo-methyl-(5')-nonbornen-2'-endo-p-nitrobenzoate **11d**

20,0 g (01, mol) **11a** were treated with 20,5 g (0, 11 mol) p-nitrobenzoyl chloride in 200 ml dry pyridine at 30-35°C and after allowing to stand for 12 hrs. at room temparature worked up as in the prepartion of tosylates. Recrystallisation from petrol ether 60-70°C yielded 20,9 g (60%) **11d** m.p. 175-176°C. $C_{21}H_{19}O_4N$ (349,4) requires C 72,19, H 5,48, N 4,01; found C 72,24, H 5,65, N 3,96.

IR-Spectrum (KBr): 1720, 1610, 1520, 1450, 1350, 129 1120, 1100 cm^{-1}.

NMR-Spectrum ($CDCl_3$); τ =1,54-1,90 (m, 4H0; 2,60-2,96 (m, 4H); 6,67-6,76 (m, 1H) ; 7,05-7,43 (m, 2H); 7,96-8,17 (m, 1H); 8,68 (s, 3H) ; 9,00-10,00 (m, 4H)

Spiro-cycolopropane -1.3'-1'-methyl-(5'.6')-benzo-norbornen-2'-yl-acetates **12c** and **14c**

17,5 g (50 mmol) **11b** and 12,0 g (30 mmol) anhydrous sodium acetate were dissolved in 1 litre glacial acetic acid and heated under reflux for 100 hrs. After cooling to room temparature, most of the glacial acetic acid was distilled off and the residue was poured in ice water and extracted repeatedly with ether. The combined ether extracts were washed with sodium bicarbonate solution, dried over sodium sulphate and ether removed. Column chromatography of the residue (silica gel, benzene/petrol ether 1:1) gave 10,0 g of the starting material **11b**. With benzene/ether 1:1 as eluent, 3,0 (70% based on converted ester) of an acetate mixture was obtained. Gas chromatography of this mixture (Carbowax 20-M, 190°C) showed the presence of three components in the ratio of 2:1:6. The second and third components were isolated by preparative g.l.c. and identified as the isomeric acetates **12c** and **14c**.

NMR-Spectrum of **12c** ($CDCl_3$) τ = 2,77-3,10 (m, 4H); 5,58-5,70 (d, J=5,0 Hz., 1H); 7,55-7,78 (m, 1H); 8,02 (s, 3H); 8,55 (s, 3H); 9,25-9,80 (m, 4H).

NMR-Spectrum of **14c** ($CDCl_3$) τ = 2,80-3,07 (m, 4H); 4,90-5,05 (m, 1H); 7,58-7,70 (m, 2H); 7,86-8,12 (dd, J= 11Hz., 2H); 8,20 (s, 3H); 8,48 (s, 3H); 8,88-10,02 (m, 4H).

Spiro-cyclopropane 1.3'-1'-methyl-(5'.6')-benzo-(5') -norbornen-2'-exo-p-toluenesulfonate **12b**

100 mg (0,5 mmol) **12a** in 5 ml absolute pyridine were treated with 110 mg (0,55 mmol) p-toluenesulfonyl chloride as before. Recrystallization from pentane gave 145 mg (83%) **12b**, m.p. 83-85°C (decomp.). $C_{21}H_{22}O_3S$ (354,3) requires C 71,18 H 6,29, S 8,93; found C 71,21, H 6,29, S 8,93.

IR-Spectrum (KBr) : 1600, 1460, 1370, 1200, 1180 cm^{-1}. NMR-Spectrum ($CDCl_3$): τ=2,12-2,82 (q, J=27 Hz., J' =8 Hz., 4H); 2,83-3,01 (m, 1H); 8,63 (s, 3H); 9,93-10,10 (m, 4H).

Spiro-cyclopropane-1.3'-1'-methyl-(5'.6')-benzo-(5') -norbornen-2'-one **13**

300 mg (1,5 mmol) **12a** were dissolved in 20 ml ether, 1,0 ml of sodium dichromate-sulphuric acid solution[10] were added and stirred for 3 hrs. at room temparature. The organic phase separated, aqeous layer extracted twice with 10 ml ether, the combined ether extracts were washed with $NaHCO_3$ solution, dried over Na_2SO_4 and ether removed under vacuum. Distillation at 10 torr and 150-180°C bath temparature yielded 180 mg (62%) **13**. $C_{14}H_{14}O$ requires C 84,81, H 7,12; found C 84,76, H 7,20.

IR-spectrum (film) : 1760, 1460 cm^{-1}.

NMR-Spectrum ($CDCl_3$) : τ = 2,68-3,12 (m, 4H); 7,10-7,28 (m, 1H); 7,50-7,64 (m, 2H); 8,48 (s, 3H); 8,64-9,65 (m, 4H).

Spiro-cyclopropane. 1.3' – 1'methyl- (5'.6')-benzo-(5')-norbornen-2-endo-ol **14a**

100 mg (0,5 mmol) **13** were reduced with 20 mg (ca. 0,5 mmol) lithium aluminiumhydride in 20 ml absolute ether and after 3 hrs. worked up as usual. Distillation (10 torr, 120-130°C bath temparature) gave 95 mg (91%) **14a**. $C_{14}H_{16}O$ requires C 83,94, H 8,05; found C 83,77, H 8,10.

IR-Spectrum (KBr) : 3260, 1450, 1440, 1380, 1270 cm^{-1}

NMR-Spectrum ($CDCl_3$): τ =2,87-3-37 (m, 4H); 6,286,37 (m, 1H); 7,53-7,68 (m, 1H); 7,93-8,10 (m, 1H); 8,35-8,87 (m, 4H); 8,97-9,80 (m, 4H).

Spiro-cyclopropane-1.3'-1'-methyl-(5'.6')-benzo-(5') -norbornen-2'-endo-p-toluenesulfonate **14b**

80,0 mg (0.4 mmol) **14a** in 5,0 ml absolute pyridine were treated with 100 mg (ca. 0,5 mmol) p-toluenesulfonyl chloride as before. Recrystallization from petrol ether 40-60°C gave 100 mg (70%) **14b**, m.p. 90-91°C. $C_{21}H_{22}O_3S$ (354,3) requires C 71,18, H 6,21, S 9,04; found C 71,28, H 6,33, S 8,75.

IR-spectrum (KBr) : 1600, 1460, 1440, 1370, 1200, 1180 cm^{-1}.

NMR-spectrum ($CDCl_3$) : τ = 2,18-2,74 (q, J=23 Hz., J' =8Hz. 4H); 2,74-3,07 (m, 4H); 5,12-5,20 (m, 1H); 7,35-7,68 (m, 4HO; 7,90-8,14 (dd, J=7 Hz., 1H); 8,37-8,95 (m, 4H); 9,12-9,90 (m, 4H).

Product analysis in the solvolysis of **12b** and **14b**

100 mg each of **12b** and **14b** were solvolysed as before and after work up, the major components **12a** and **14a** were isolated by preparative g.l.c and their spectroscopic data compared with those of the authentic samples. The composition of the solvolysis mixture is given in table-2.

Kinetic measurements:

The method used for the measurement of reaction rates and the apparatus is the same as described previously [4]. The rate constants and the activation parameters are summarized in table-1.

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