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Polar Effects of 4-Substituents in the Solvolysis of Tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecan-11-yl Triflates. Through-Space vs. Inductive Model

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4-Substituted tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecan-11-yl derivatives **7** were obtained starting from the corresponding derivatives **8a – c**. Solvolyses of the 11-triflate of the parent compound and of five triflates with substituents at C-4 (X = CH_3, F, OAc, SC_6H_5, and OCH_3) were studied in 60% aq. acetone and in 97% hexafluoroisopropyl alcohol (HFIP). Results are compared with those obtained for other aliphatic systems like **1**, **2**, and **3**. The relative importance of through-space and inductive effects is discussed. Transmission of polar effects in **7** can be explained by either model.

Polare Effekte von 4-Substituenten bei der Solvolyse von Tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecan-11-yl-triflaten. Through-space-Effekt im Vergleich zum induktiven Effekt

4-Substituierte Tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecan-11-yl-Derivate **7** wurden ausgehend von den entsprechenden Olefinen **8a – c** dargestellt. Die Solvolyse des 11-Triflats der unsubstituierten Verbindung sowie die von fünf C-4-substituierten Triflaten (X = CH_3, F, OAc, SC_6H_5 und OCH_3) wurde in 60proz. wäßrigem Aceton und in 97proz. Hexafluorisopropylalkohol (HFIP) untersucht. Die Ergebnisse werden mit denen der bekannten aliphatischen Systeme wie **1**, **2** und **3** verglichen. Die Bedeutung von through-space- im Vergleich zu induktiven Effekten wird diskutiert. Die Übertragung polarer Effekte bei der Verbindungsreihe **7** kann mit beiden Modellen beschrieben werden.

Transmission of polar substituent effects has been described by two models, the through-space (field) effect[2] and the inductive model[3]. The field model has been claimed to be superior to the inductive model[3,4]. The effect of polar substituents X on the solvolysis rates has been investigated in various aliphatic systems[5]. E. g., marked effects have been observed with aliphatic sulfonates **1**[6], the polycyclic compounds **2** and **3**[7,8], 2-norbornyl systems **4**[9] and **5**[10], and one of the bromides in the longifolen series **6**[11].

In general, after the solvolyses data are correlated by LFER[12], the magnitude of the reaction constant and the deviations from the correlation line have been used to discuss the specific mechanism.

The mechanism of solvolysis of systems like **1**, **4**, and **6** can be complicated, since various degrees of nucleophilic solvent assistance as well as anchimeric assistance might be involved. Therefore, we have chosen a system expected to be free of nucleophilic solvent assistance and have studied solvolyses of the 4-substituted 11-triflates of tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecane (**7**).

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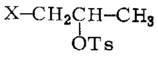
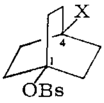
In the following we use the generally accepted nomenclature[15] for the assignment of the three isomeric tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecanes. The prefixes *endo,endo, endo,exo,* and *exo,exo* are related to the configuration of the fusion of the two norbornane units, e.g. compounds **7** are the triflates of *exo*-4-X-*endo,exo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecan-*anti*-11-ol.



$X{-}CH_2\underset{\displaystyle OTs}{C}H{-}CH_3$

1



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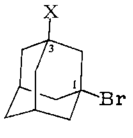

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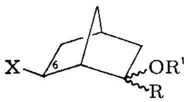

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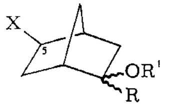

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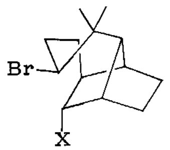
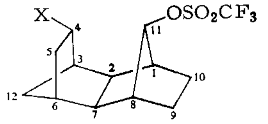


6



7

Solvolysis of the 11-brosylate of the parent system in acetic acid has already been studied by *Winstein* et al.[13].

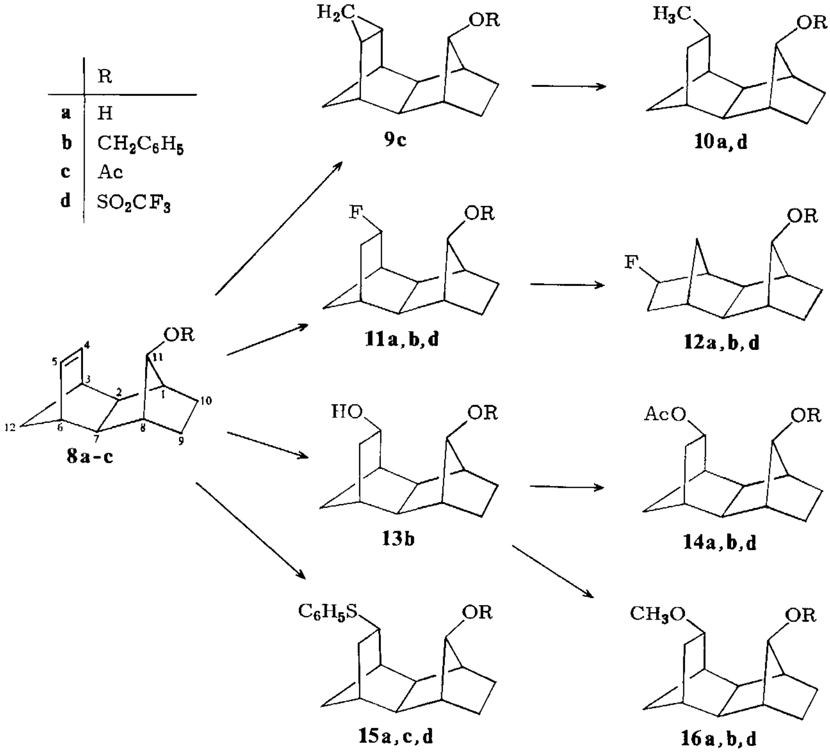
Synthesis

The synthesis employed for six differently 4-substituted derivatives of **7** starts from the tetracyclic olefin **8a** (see Scheme 1). **8a** was prepared from hexachlorocyclopentadiene and *anti*-7-norbornenyl acetate in a two-step synthesis[14]. Recently, we reported an alternative route to **8a** as well as a synthesis of the tetracyclic compounds **10** and **14**[15].

In general, synthesis of 4-substituted tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecanes make use of nonionic additions of various reagents to the double bond of **8a – c** (see Scheme 1). Ionic conditions should be avoided since they give mainly rearranged products with tetracyclic *exo,exo*-structures[16]. For example, addition of HF-reagent in pyridine[17] to the double bond of olefin **8b** leads to a 6:4 mixture of the isomeric fluorides **11b** and **12b**. But all other reactions applied (see Scheme 1) proceed without rearrangement yielding the desired *exo,endo*-tetracyclic products. Hydroboration-oxidation of olefin **8b** gives the alcohol **13b**, which was acetylated to product **14b** or methylated by CH_3I/NaH yielding methyl ether **16b**. Radical addition of thiophenol to olefin **8c** (photolytic conditions) yields thioether **15c**. All reactions give relatively good yields, 60 – 80%; all new products were fully characterized by standard spectroscopic techniques.

Alcohols **10a, 11a, 12a, 14a, 16a,** and the unsubstituted alcohol **17a** were converted into the corresponding triflates by treatment with triflate anhydride[18]. Solvolysis rates of triflates were easily measured in the 25 – 100°C temperature range (see below).

Scheme 1



	R
a	H
b	$CH_2C_6H_5$
c	Ac
d	SO_2CF_3

Solvolysis

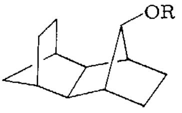
Solvolysis rate measurements of the parent triflate **17c** and of substituted compounds **10d**, **11d**, **14d**, **15d**, and **16d** were performed in 60% aqueous acetone and in 97% HFIP (hexafluoroisopropyl alcohol). The former solvent exhibits a strong nucleophilicity with medium ionising power while the latter shows very low nucleophilicity but strong ionising power[19]. The reaction was followed at three temperatures by the conductance method. Solvolysis rates of the fluorine compound **11d** were determined using a mixture of isomers **11d** and **12d**; the latter was inert under those conditions. Tables 1 and 2 summarize the results.

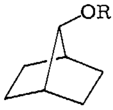
Results and Discussion

Solvolysis of the 11-brosylate (**17b**) of tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecane exhibited rate enhancement of ca. 100 in acetic acid at 25 °C compared to 7-norbornyl brosylate (**18a**)[13]. A rate enhancement of ca. 60 is calculated for triflate **17c** compared to 7-norbornyl triflate (**18b**) in 60% acetone at 80 °C (see Table 1).

Since the rear of the reaction center in sulfonates **17b, c** is shielded by the ethylene bridge of the molecule solvent assistance[19] can be excluded. But two assisted pathways

	R
17a	H
b	OBs
c	SO_2CF_3



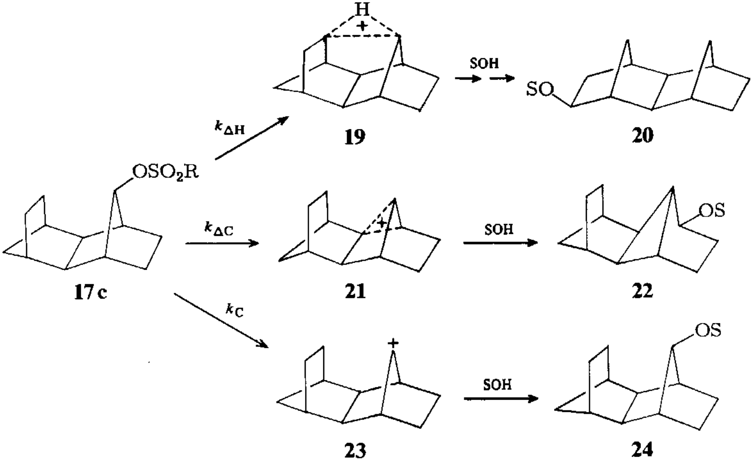


	R
18a	Bs
b	SO_2CF_3

Bs = $4\text{-}BrC_6H_4SO_2$

($k_{\Delta H}$ and $k_{\Delta C}$) as well as unassisted behaviour (k_C) can occur in solvolysis of the parent sulfonate and the 4-derivatives (see Scheme 2).

Scheme 2



Winstein has attributed the rate enhancement of **17b** as well as the observation of rearranged product **20** to the existence of the H-bridged intermediate **19**[13]. But we have recently demonstrated that such accelerations can be attributed to steric effects[15]. The rate acceleration of **17** can be described by a relationship employing the calculated strain energy difference ΔH (cation) − ΔH (hydrocarbon) applied by *Harris*[20] for such systems. Therefore, we believe that bridged intermediates like **19** do not play an important role in normal solvolyses of sulfonates **17** and the reactions proceed mainly by a k_c-mechanism. Structure **19** can be regarded as a bridged cyclodecylstructure. For symmetrical cations of this size *Sorensen* has deduced a nonclassical structure in superacid solvents[20a]. But the H-bridged structure in **19** is unsymmetrical and, therefore, expected to be less stable.

The rates of all six triflates in Table 1 can be correlated by LFER using the Taft relationship[12,21] well established for aliphatic systems (see Fig. 1). In 60% acetone at 75°C a reaction constant of -0.95 (correlation coefficient 0.996) is calculated while in 97% hexafluoroisopropyl alcohol (HFIP) at 25°C the absolute value of the reaction constant is much larger, -2.11 (correlation is less satisfactory, c.c. 0.980). A correlation is also obtained by using *Grob's* σ_q^I-values[5]. In 60% acetone the reaction constant is -0.398 (c.c. 0.945), in 97% HFIP a value of -0.944 (c.c. 0.985) is obtained[21].

Table 1. Solvolysis Data of Triflates **7** in 60% Acetone

Compound	T °C	k [a] s^{-1}	$\Delta H^{\ddagger}$ $\frac{kcal}{mol}$	$\Delta S^{\ddagger}$ $\frac{cal}{mol \cdot Grad}$	k_{rel} (75°C)
X = H	29.90	1.054×10^{-4}			
(17c)	40.00	4.030×10^{-4}			
	50.00	1.269×10^{-3}			
	75.00[b]	1.924×10^{-2}	23.5	0.8	1
	80.00	3.156×10^{-2}			
X = SPh	35.00	5.769×10^{-5}			
(15d)	46.20	2.277×10^{-4}			
	59.95	1.082×10^{-3}			
	75.00[b]	5.191×10^{-3}	23.3	−2.3	2.69×10^{-1}
X = CH_3	20.00	6.028×10^{-5}			
(10d)	30.35	2.236×10^{-4}			
	40.80	7.672×10^{-4}			
	75.00[b]	2.621×10^{-2}	21.8	−3.6	1.32
X = OCH_3	46.80	3.219×10^{-4}			
(16d)	58.50	1.416×10^{-3}			
	70.00	4.743×10^{-3}			
	75.00[b]	8.313×10^{-3}	24.7	2.5	4.32×10^{-1}
X = $OCOCH_3$	50.00	1.387×10^{-4}			
(14d)	62.50	7.805×10^{-4}			
	75.10	2.615×10^{-3}			
	75.00[b]	2.782×10^{-3}	25.5	2.8	1.45×10^{-1}
X = F	58.00	4.894×10^{-4}			
(11d)	69.95	1.189×10^{-3}			
	83.00	3.665×10^{-3}			
	75.00[b]	1.913×10^{-3}	18.2	−19.0	9.94×10^{-2}
18b	80.00[c]	5.670×10^{-4}			1.79×10^{-2}

[a] Average value for two or three measurements. – [b] Calculated from values at other temperatures. – [c] *X. Creary,* J. Am. Chem. Soc. **98**, 6608 (1976).

Table 2. Solvolysis Data of Triflates 7 in 97% (vol./vol.) Hexafluoroisopropyl Alcohol (HFIP)

Compound	T °C	k [a] s^{-1}	$\Delta H^{\ddagger}$ $\frac{kcal}{mol}$	$\Delta S^{\ddagger}$ $\frac{cal}{mol \cdot Grad}$	k_{rel} (25°C)
X = H	0.20	4.016×10^{-4}			
(17c)	17.10	2.993×10^{-3}			
	25.00[b]	7.256×10^{-3}	18.4	−6.7	1
X = CH_3	0.20	1.189×10^{-3}			
(10d)	17.50	8.141×10^{-3}			
	25.00[b]	1.751×10^{-2}	17.0	−9.6	2.41
X = SPh	27.60	4.886×10^{-4}			
(15d)	33.00	8.752×10^{-4}			
	42.50	2.345×10^{-3}			
	25.00[b]	3.653×10^{-4}	19.2	−9.7	5.03×10^{-2}
X = OCH_3	38.25	6.597×10^{-4}			
(16d)	48.60	1.981×10^{-3}			
	25.00[b]	1.447×10^{-4}	20.5	−7.3	1.99×10^{2}
X = $OCOCH_3$	40.75	5.023×10^{-4}			
(14d)	50.00	1.066×10^{-3}			
	65.20	4.039×10^{-3}			
	25.00[b]	1.050×10^{-4}	17.4	−18.3	1.46×10^{-2}
X = F	69.40	3.513×10^{-3}			
(11d)	59.95	1.551×10^{-3}			
	49.80	6.637×10^{-4}			
	25.00[b]	5.865×10^{-5}	10.0	−17.5	8.08×10^{-3}

[a] Average value for two or three measurements. – [b] Calculated from values at other temp.

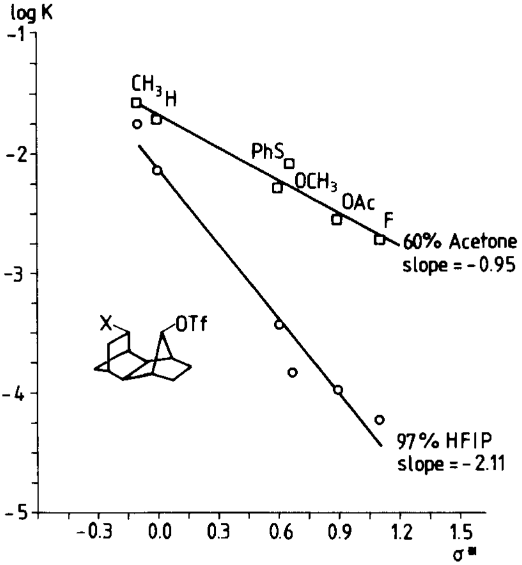


Fig. 1. Taft-Treatment of Triflates **7** (see Table 1; HFIP = Hexafluoroisopropyl Alcohol)

From these results a graded mechanism seems very likely in the solvolyse of the whole series of triflates **7**. Participation can cause marked deviation from LFER as found in systems like **6**[11]. The products agree with this conclusions. Hydrolysis of triflate **14d** gave the corresponding alcohol exclusively[22].

Magnitude of Reaction Constants in Solvolysis Reactions of Various Aliphatic Systems

The magnitude of the reaction constant observed in the solvolysis of aliphatic systems is expected to reveal some indications about the details of transmission mode and the specific mechanism involved. In Table 3 we have summarized some of the results obtained from solvolysis reactions in systems of type **1**, **2** and **3** to compare with **7** investigated here.

It is apparent that the values of the reaction constants of solvolysis reactions strongly depend on the solvent. E. g., for the aliphatic system **1** the value increases from -2.32 in acetic acid via -7.2 (TFA) to -9.1 in 97% HFIP, a very strongly nonnucleophilic solvent (see Table 3). But the mechanism changes in the aliphatic system **1** by change of the solvent; in acetic acid solvolysis occurs mainly by a solvent assisted pathway (k_s) while in the less nucleophilic solvents mentioned above limiting behavior (k_c) is approached.

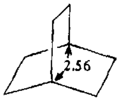
The dielectric constants of the solvents increase in the same order. It is likely that the solvent nearly spherically surrounds acyclic systems like **1**. In polycyclic compounds like **2**, **3**, and **7** one half of the molecule is "protected" by the cage and solvation can occur half-spherically. The increase of the reaction constant in going from normal solvent to 97% HFIP, therefore, could be markedly different in systems **1** and **7**. The same solvent dependence as found in **7** should be observed in other caged systems like **2** and **3** and study of solvolysis of these systems in nonnucleophilic solvents like HFIP seems desirable[22].

Table 3. Reaction Constants (Using Taft's σ^* Values) Obtained for Aliphatic Systems **1**, **2**, **3**, and **7**

Series	Kind of Substituents	Conditions	ρ^*
1[a]	alkyl- and aryl groups	acetic acid, 100°C	−2.32
1[a]	alkyl- and aryl groups	formic acid, 25°C	−3.38
1[b]	electronegative groups	acetic acid, 75°C	−3.42
1[c]	alkyl groups	TFA, 25°C	−7.21
1[d]	alkyl groups	97% HFIP, 25°C	−9.10
2[e]	various groups	80% ethanol, 100°C	−2.32
3[e]	various groups	80% ethanol, 100°C	−2.70
7[f]	electronegative groups	60% acetone, 75°C	−0.95
7[f]	electronegative groups	97% HFIP, 25°C	−2.11

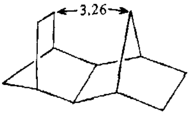
[a] *J. C. Lancelot, J. J. Harper,* and *P. v. R. Schleyer,* J. Am. Chem. Soc. **91**, 4294 (1969). – [b] *J. J. Harper,* Thesis, Princeton University 1967. – [c] *P. E. Peterson, R. E. Kelley, R. Betholi,* and *K. A. Sipp,* J. Am. Chem. Soc. **87**, 5169 (1965). – [d] *T. W. Bentley, C. T. Bowen, W. Parker,* and *C. J. Watt,* J. Am. Chem. Soc. **101**, 2486 (1979); *T. W. Bentley, C. T. Bowen, D. H. Morton,* and *P. v. R. Schleyer,* ibid. **103**, 6466 (1981); *D. Lenoir,* unpublished results. – [e] *P. v. R. Schleyer* and *C. W. Woodworth,* J. Am. Chem. Soc. **90**, 6528 (1968). – [f] This work.

It is of interest to compare the relative magnitude of the reaction constants in the three polycyclic systems **2**, **3**, and **7** with the calculated distance between the carbon bearing the substituent X and the carbon at the reaction center (values are obtained for the parent hydrocarbon using force field calculations):



2

3

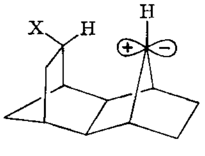


7

In **2** and **3** this distance is nearly the same, in **3** the distance is only 30% larger compared to **2** and **3**. The reaction constant ρ^* of −0.95 observed in 60% acetone is much smaller compared to those observed in **2** (−2.30) and **3** (−2.70) (80% ethanol). Only the reaction constant of −2.10 observed for **7** in 97% HFIP is of similar size. Therefore, one has to conclude that in **7** the through space interaction is less efficient as in **2** and **3**. The bonding situation in tetracyclic system 7 is significantly different compared to **2** and **3**.

In cation **25** there are two hydrogens between the substituent X and the reaction center while in the bicyclic cation **26** a direct interaction between the orbitals at C-4 and C-1 is possible.

In bicyclic cation **26** the dominance of the through space effects has been substantiated by ab initio calculations[23]. The effect of five groups, X = CH_3, $C\equiv CH$, OH, F, and CN on the stability of bridgehead cation **26** were calculated and compared to those of an appropriate model with the same spatial relationships but without σ-bonding framework[23]. In addition, recent ab initio calculations of proton affinity of aryl substituted alkylamines show the dominance of the field model[24].



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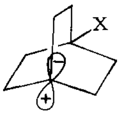

26

Grob has demonstrated experimentally the existence of a through space effect in solvolytic reactions[24a].

The possible operation of an inductive effect can be tested in the following way. There are three main transmission modes by σ-bonds between C-4 and C-11 in cation **25**; one way by four σ-bonds and two ways by five bonds. The reaction constants for the solvolyses of triflates **7** in 97% HFIP can be calculated using the reaction constant of −9.1 determined for aliphatic sulfonates **1** and applying three different fall-of factors (see Table 4).

Table 4. Calculated and Experimental Reaction Constants for **7** Using three Different Fall-of Factors[a]

0.65[a]	0.40[a]	0.20[a]	σ observed
−1.00	−0.12	−0.006	−0.97 (60% acetone)
−2.68	−0.33	−0.02	−2.11 (97% HFIP)

Assuming the generally accepted[25] fall-off factor of 0.65, the inductive model described the effect of substituents in **7** fairly well.

Conclusions: The results show that both models – the inductive and the field-effect model – have arbitrarily chosen premises, but either can be used to describe polar substituent effects.

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Experimental Part

Melting points: Tottoli apparatus, sealed capillaries. – ^1H NMR spectra: in $CDCl_3$ solution, TMS internal standard, Varian A-60 A spectrometer. – IR: Perkin Elmer, Mod. 177. – Mass spectra: CH 5 spectrometer of Varian Mat.

endo,exo-Tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-en-anti-11-ol (**8a**) was prepared from hexachlorocyclopentadiene and *anti*-7-norbornenyl acetate and subsequent dechlorination according to the method described by *Battiste*[14]. An alternative synthesis of **8a** was recently described by us[15].

anti-11-Benzyloxy-endo,exo-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-4-ene (**8b**): Alcohol **8a** (15.0 g, 85.2 mmol) was stirred with 9.55 g of powdered KOH and 21.6 g of benzyl chloride for 24 h at 100 °C. After cooling 200 ml of ether was added and the mixture was refluxed for 2 h. The organic phase was decanted and the solvent evaporated. The resulting mixture was destilled in vacuo to remove the unreacted chloride. The crude mixture was chromatographed on silica gel with pentane as eluent; benzyl chloride was eluted first. The crude product was crystallized several times from methanol; 9.08 g (40%) of a white solid was obtained, m. p. 99 – 101 °C. – NMR: δ = 0.78 – 1.97 (m), 2.78 (3,6-H), 4.45 (11-H), 5.90 (dd, 4,5-H), 7.15 (phenyl). – MS: *m/e* = 266 (M^+, 1%), 175 (10), 147 (13), 119 (13), 105 (12), 93 (19), 92 (100), 81 (25), 79 (39), 77 (12), 67 (31), 65 (22).

anti-11-Benzyloxy-exo-4-fluoro-endo,exo-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecane (**11b**) *and exo,exo-Isomer* (**12b**): To a solution of 2 ml of $(HF)_x$ reagent in pyridine[26] 0.30 g of olefin **8b** dissolved in 2 ml of THF was added and the mixture was stirred for 12 h at 0 °C. The product was poured onto ice and extracted with ether. The ether phase was washed with 10% HCl, $NaHCO_3$, and NaCl solution. After drying over $MgSO_4$, the solvent was evaporated in vacuo yielding 0.31 g of a crude yellow compound. GLC revealed a 6 : 4 mixture of **11b** and **12b**. The crude mixture was dissolved in 100 ml of ethanol and hydrogenated in the presence of 50 mg of Pd/C catalyst during 16 h. The catalyst was filtered and the solvent evaporated yielding 0.13 g (85%) of a mixture of **11a** and **12a**. – NMR: δ = 4.45 (4-H of **11a**, J_{HF} = 53 Hz), 4.62 (11-H of **12a**), 3.69 (4-H of **12a**, J_{HF} = 36 Hz), 0.81 – 2.73 (m). – MS: *m/e* = 196 (M^+, 7%), 178 (15), 177 (5), 176 (21), 167 (5), 165 (43), 91 (100), 79 (98), 67 (93).

exo-4-Methoxy-endo,exo-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecan-anti-11-ol (**16a**): 0.47 g of **13b**[15] (2.0 mmol) was methylated by treatment with 0.57 g (4.0 mmol) of methyl iodide in the presence of 0.050 g (2.08 mmol) of NaH. After usual work-up 0.48 g (80%) of a colourless solid (**16b**) was obtained, which was directly converted into the 11-OH compound: 0.28 g (0.94 mmol) of **16b** were hydrogenated in 10 ml of ethanol in the presence of 0.05 g of Pd/C catalyst during 15 h. After usual work-up the product was sublimed in vacuo yielding 0.11 g (56%) of **16a** as a colourless solid, m. p. 60 – 62 °C. – NMR: δ = 0.93 – 2.50 (m), 3.27 (OCH_3), 3.57 (4-H), 4.24 (11-H). – MS: *m/e* = 208 (M^+, 35%), 190 (12), 176 (41), 148 (48), 147 (10), 145 (11), 125 (18), 119 (26), 117 (14), 97 (22), 96 (100), 91 (30).

$C_{13}H_{20}O_2$ (208.2) Calcd. C 74.96 H 9.68 Found C 74.73 H 9.36

anti-11-Acetoxy-exo-4-(phenylthio)-endo,exo-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecane (**15c**): 9.0 mmol of acetate **8c**[15] and 0.79 g (6.9 mmol) of thiophenol, dissolved in 50 ml purified *n*-pentane, were irridiated with a Hanovian lamp during 3 h. The solvent was evaporated and the product crystallized from methanol several times yielding 0.90 g (39%) of pure **15c** as a colourless solid, m. p. 71 – 72 °C. – NMR: δ = 0.90 – 2.43 (m), 2.02 ($COCH_3$), 3.72 (4-H), 5.23 (11-H), 7.32 (phenyl). – MS: *m/e* = 328 (M^+, 4%), 327 (12), 326 (29), 218 (28), 178 (16), 177 (100), 169 (52), 168 (19), 152 (11), 116 (12).

$C_{20}H_{24}O_2S$ (328.2) Calcd. C 73.15 H 7.36 Found C 73.03 H 7.38

exo-4-(Phenylthio)-endo,exo-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecan-anti-11-ol (**15a**): 0.75 g of acetate **15c** was refluxed in a mixture of 50 ml of methanol, 20 ml of water, and 1.0 g of NaOH during 3 h. The mixture was poured onto 200 ml of H_2O and the product was isolated by extraction with ether. After usual work-up the product was crystallized from methanol, yielding 0.38 g (58%) of pure **15a**, m. p. 117 – 118 °C. – NMR: δ = 0.90 – 0.60 (m), 3.58 (4-H), 4.48 (11-H), 7.32 (phenyl). – MS: 286 (M^+, 54), 177 (53), 159 (12), 133 (13), 110 (100), 93 (25), 91 (23), 81 (13), 79 (16), 67 (32).

$C_{18}H_{22}OS$ (286.3) Calcd. C 75.48 H 7.74 Found C 75.47 H 7.53

Compounds **9c**, **10a**, **13b**, and **14a, b** were prepared according to the described procedures[15].

Solvolyses of Triflates

The triflates of the alcohols **8a**, **10a**, **11a**, **15a**, and **16a** were prepared by the procedure of *Streitwieser*[18]; yields are in the range of 80%. In the NMR spectra of all triflates the 11-H signal is shifted downfield by 1 ppm compared to the corresponding alcohol. Products were crystallized twice from pentane shortly before use.

Acetone p. a. was purified by the standard procedure, hexafluoroisopropyl alcohol (HFIP) was carefully destilled from P_2O_5 in a 90 cm Vigreux column. HFIP solution (97%) means vol (vol) with H_2O as second component).

Kinetics: Conductance was followed with ca. 10^{-4} M solutions of triflates during 4 half lives using a Wayne-Kerr Bridge, Mod. 642, capable of 0.1% accuracy. The conductivity cells used had bright platinum electrodes, cell constants 0.2 – 0.4 and held ca. 20 ml. Constant temperature baths (Haake Thermostat) with 0.05°C deviations were used. Rate constants were calculated by using DeTar's LSKIN computer program[27].

Product Studies: 2 mg of either triflate was heated during 8 half-lives in 60% acetone, buffered with 2,6-lutidine. The products were extracted with pentane/$CHCl_3$ (4 : 1) and after usual work-up subjected to GLC (capillary column UCON HB, 20 m). Triflate **17c** yielded one peak identical with rearranged *exo,exo*-alcohol. **10c** gave a mixture of 5 products, the main product (48.8%) being identical with **10a**, the other compounds (16.2, 18.2, 10.8, and 6.1%) were not identified. **14d** gave **14a** exclusively as shown by coinjection of authentic material.

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