endo,endo- and *exo,exo*-Bicyclo[1.1.0]butane-2,4-dimethanol Dimesylate: Synthesis, Structure and Solvolysis

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Dedicated to Professor Thomas J. Katz (Columbia University) with appreciation for the bounteous benzvalene synthesis he has designed

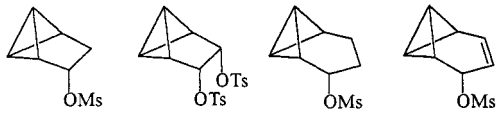
Keywords: Bicyclobutylcarbinyl sulfonates / Carbocations / Kinetics of solvolysis / Neighbouring-group effects / Strained molecules

The title compounds *endo,endo*-**9** and *exo,exo*-**9** were prepared from benzvalene. As determined by single-crystal X-ray diffraction, several geometrical parameters of *endo,endo*-**9** are particularly remarkable, namely the large interflap angle of the bicyclo[1.1.0]butane system (128.2°) and the length of the C-1–C-3 bond (151.2 pm). Solvolyses of *endo,endo*-**9** in 60% acetone/water, ethanol and 2,2,2-trifluoroethanol gave rise mainly to *cis*-5-substituted cyclopent-2-ene-1-methanol mesylates (*cis*-**10**, *cis*-**11**). Small quantities of the corresponding *trans* isomers (*trans*-**10**, *trans*-**11**) suggest a configurational conversion of the intermediate, which is proposed to be the nonclassical *pseudoaxial* 2-mesyloxymethyl-substituted cyclopent-3-en-1-yl cation (*ax*-**31**) formed from *endo,endo*-**9** by heterolytic dissociation accompanied by a Wagner-Meerwein rearrangement. The solvolyses of *exo,exo*-**9** took an entirely different course and afforded non-rearranged products (**26**, **27**) exclusively. This is interpreted in terms of the stereochemical requirements of the Wagner–Meerwein rearrangement, which in the case of *exo,exo*-**9** would result in a highly strained cation such as **32** or **33**. In consequence, the generation of the bicyclobutylcarbinyl cation **34** seems to be the most favourable alternative. This result, together with kinetic data for solvolyses of *endo,endo*-**9** and *exo,exo*-**9**, casts doubt on a report on solvolyses of the dimethylbicyclo[1.1.0]but-2-ylcarbinyl tosylates **6**.[4] Solvolyses of *endo,endo*-**9** in several solvents are about 5 times faster than those of the ditosylate **2** (or the corresponding dimesylate), a less flexible bicyclo[1.1.0]butane derivative. That the solvolysis of *exo,exo*-**9** takes place about 8 times more slowly than *endo,endo*-**9** is interpreted by invoking a weaker σ-participation in the case of the former. In comparison to the stereochemically closely related *exo,exo*-**9**, the cyclobutanedimethanol ditosylate **28** solvolyses only 50 times more slowly.

Introduction

In two detailed investigations,[1,2] we have studied the influence of the bicyclo[1.1.0]butane system on the rate of the heterolytic dissociation of bicyclo[1.1.0]but-2-ylcarbinyl esters. Substrates were the tricyclic sulfonates **1**−**4** depicted in Scheme 1.

Initial work[1] was greatly facilitated by the introduction of a second sulfonate ester group adjacent to the first one (as in **2**) to stabilise the highly labile bicyclobutane group, and to reduce the solvolytic reactivity by a factor of ca. 3 × 10^3 [e.g. compare rate constants for **1** and **2** (Scheme 1), with mesylates (OMs) and tosylates (OTs) being about equally reactive[3]].



	1	**2**	**3**	**4**
k/s^{-1}	3.5×10^{-2}	1.3×10^{-5}	3.0×10^{-1}	5×10^{3}

Scheme 1. Rate constants for the solvolysis of bicyclo[1.1.0]but-2-ylcarbinyl sulfonates in 80% v/v ethanol/water at 25 °C from ref.[1] (**1**, Table 4; **2**, Table 3) and ref.[2] (**3** and **4**, Table 1)

Solvolytic reactivities of the bicyclobut-2-ylcarbinyl tosylates **5** and **6** (Scheme 2),[4] and the bicyclobut-1-ylcarbinyl system,[5] both lacking the bridge connecting the *endo* positions, have been investigated previously. While no product structures were published in the case of the substrates **5**, tosylates *endo*-**6** and *exo*-**6** were both reported to furnish mainly 1,3-dimethylcyclopent-3-en-1-ol (**7**) on hydrolysis in 80% v/v dioxane/water at 25 °C. The rate constants at 25 °C (2.71 × 10^{-4} and 5.63 × 10^{-4} s^{-1} for *endo*-**6** and *exo*-**6**, respectively) appear to indicate that these compounds do not solvolyse more rapidly than cyclopropylcarbinyl tosylate.[4] In contrast, approximate kinetic studies of bicyclobu-

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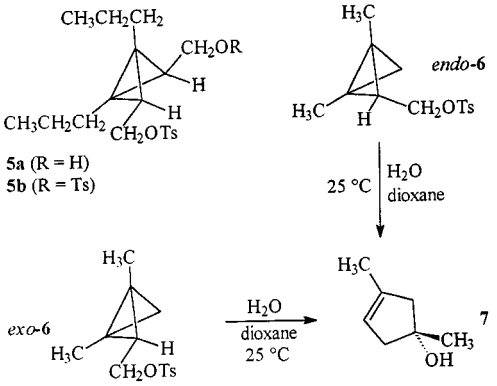
tane-1-methanol *p*-nitrobenzoate indicated that it solvolysed at least 1000 times more rapidly than cyclopropylcarbinyl *p*-nitrobenzoate.[5]



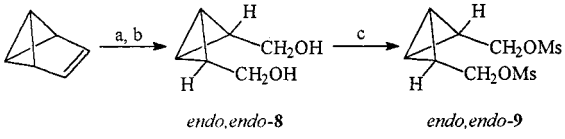
Scheme 2. Nonbridged bicyclo[1.1.0]but-2-ylcarbinyl esters solvolysed previously[4]

To provide further insights into the cationic reactivity of bicyclobut-2-ylcarbinyl systems lacking additional rings, we now report rate and product studies of the title dimesylates **9**, in which one of the two CH_2OMs groups should act as a deactivating group as well as a stereochemical label. We also report structural details of *endo*,*endo*-**9** and comparisons between the solvolytic reactivities of bicyclobut-2-ylcarbinyl and corresponding cyclobutylcarbinyl sulfonates.

Results

1. Synthesis and Structure of the Dimesylate *endo,endo*-9

The preparation of *endo*,*endo*-**9** has been reported previously.[6] Benzvalene[7] was ozonised and the ozonide reduced to give bicyclobutane-2,4-dimethanol *endo*,*endo*-**8**, which was converted into *endo*,*endo*-**9** under standard conditions (Scheme 3). Unlike in the earlier investigation,[6] *endo*,*endo*-**9** was this time obtained as a pure crystalline solid in 57% yield.



Scheme 3. Synthesis of *endo*,*endo*-**9**: a) O_3, Et_2O, −78 °C; b) $LiAlH_4$, Et_2O/THF, −78 to −30 °C; then H_2O; c) $MeSO_2Cl$, NEt_3, −30 to 0 °C

According to the X-ray structure analysis (Figure 1), *endo*,*endo*-**9** possesses C_2 symmetry in the crystal. The mutual repulsion of the substituents results in an angle of 128.2° between the three-membered rings. Hence, this interflap angle ranks among the largest of its kind. Only 2,2,4,4-tetramethyl-1,3-bis(methylsulfanyl)bicyclo[1.1.0]butane has a slightly larger value (128.6°),[8] while that of dimethyl *endo*,*endo*-1,3-diphenylbicyclo[1.1.0]butane-2,4-dicarboxylate approaches it fairly closely (127.2°).[9] However, the bicyclobutane system of these model compounds is directly attached to other functional groups, whereas that of *endo*,*endo*-**9** is free of direct electronic influences apart from the inductive effect of the nearby mesylate groups.

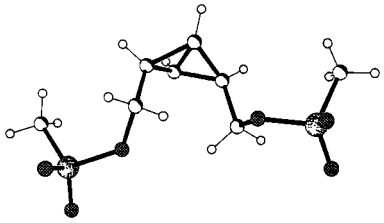
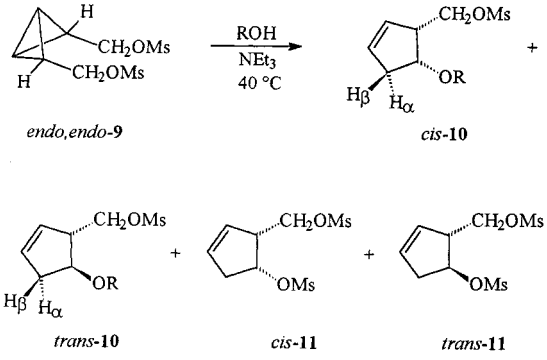


Figure 1. Molecular structure of dimesylate *endo*,*endo*-**9** as determined by X-ray diffraction

Irngartinger and Lukas[10] empirically found a linear correlation between the interflap angle and the length of the C-1−C-3 bond in bicyclobutanes; this was subsequently supported by quantum-chemical calculations.[9,11] With a value of 151.2 pm, the respective bond in *endo*,*endo*-**9** fits only qualitatively into this correlation, deviating from the original straight line by being too long by 2 pm. Compared to unsubstituted bicyclo[1.1.0]butane,[12] the central bond of *endo*,*endo*-**9** is elongated by 1.5 pm and the interflap angle increased by 6.9°, while the peripheral bonds have virtually the same length (149.8 pm).

2. Solvolyses of the Dimesylate *endo,endo*-9

Product studies of solvolyses of *endo*,*endo*-**9** were performed in three solvents: 60% v/v acetone/water (60% A), ethanol (EtOH) and 2,2,2-trifluoroethanol (TFE). The results are summarised in Scheme 4.



key for substituents	solvent	R	ratio (yield of isolated product/%) *cis*-**10** : *trans*-**10** : *cis*-**11** : *trans*-**11**
a	60% A	H	28 (59) : 1 : 2 : <1
b	EtOH	C_2H_5	25 (45) : 5 (4) : 3 : 1
c	TFE	CF_3CH_2	4 (13) : 1 : 1 : <1

Scheme 4. Products of solvolyses of *endo*,*endo*-**9**

After *endo*,*endo*-**9**, dissolved in 60% A containing triethylamine, had been warmed at 40 °C over three days, the cyclopentenol *cis*-**10a** was isolated in 59% yield. The ^1H NMR spectrum of the crude product also indicated the presence of the diastereomer *trans*-**10a** and the dimesylate *cis*-**11**, the ratio of *cis*-**10a**/*trans*-**10a**/*cis*-**11** being 28:1:2. A sample of pure *cis*-**11** was prepared by mesylation of *cis*-**10a**. Solvolysis of *endo*,*endo*-**9** in ethanol furnished the ethyl

Table 1. ^{1}H NMR spectroscopic data of 5-substituted cyclopent-2-ene-1-methanol mesylates in $CDCl_3$; chemical shifts are δ values [δ($CHCl_3$) = 7.26]; the signal multiplicities, given for *cis*-**10a** and *trans*-**10b**, are representative; the coupling constants (absolute values in Hz) were determined to be $J_{1,2}$ = 2.1, $J_{1,3}$ = 2.1−2.4, $J_{1,4\alpha}$ = 1.5−2.1, $J_{1,4\beta}$ = 1.2−2.1, $J_{1,5}$ = 3.5 (*trans*-**10**, **-11**), 6.2−7.0 (*cis*-**10**, **-11**), $J_{2,3}$ = 6.0−6.2, $J_{2,4}$ = 1.7−2.3, $J_{3,4}$ = 2.1−2.5, $J_{4,4}$ = 16.8−18.1, $J_{4\alpha,5}$ = 2.4−4.6 (*cis*-**10**, **-11**), 7.0 (*trans*-**10**, **-11**), $J_{4\beta,5}$ = 6.2−6.5 (*cis*-**10**, **-11**), 3.4−3.5 (*trans*-**10**, **-11**); coupling constants of the $CH_2OSO_2CH_3$ group: ^2J = 9.5−10.4, ^3J(coupling to 1-H) = 4.7−8.3 Hz

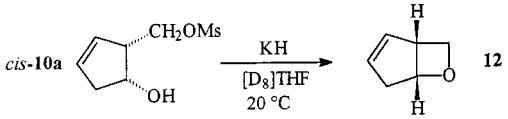
Compd.	5-Subst.	1-H	2-H	3-H	4-H$_\alpha$	4-H$_\beta$	5-H	$CH_2OSO_2CH_3$	Signals of the 5-subst.
cis-**10a**[a]	OH	3.07	5.58	5.89	2.39	2.72	4.59	4.38, 4.50, 3.05	1.91
		m	dq	dq	dtt	dddt	td	dd dd s	br. s
cis-**10b**	OC_2H_5	3.12	5.69	5.85	2.41	2.55	4.20	4.24, 4.44, 3.01	3.44, 3.55 (2 × dq, ^2J = 9.2, ^3J = 7.0 Hz), 1.18 (t)
cis-**10c**	OCH_2CF_3	3.19	5.65	5.85	2.48	2.62	4.36	4.30, 4.40, 3.00	3.83, 3.86 (2 × dq, ^2J = 12.2, $J_{H,F}$ = 8.6 Hz)
cis-**11**	OSO_2CH_3	3.32	5.66	5.92	2.74	2.83	5.39	4.38 (2 H), 3.06	3.07
trans-**10a**	OH	3.03	5.59	5.86	2.78	2.36	4.37	4.09, 4.27, 3.04	1.96
trans-**10b**	OC_2H_5	3.06	5.60	5.85	2.71	2.39	3.98	4.13, 4.20, 3.02	3.51 (q, ^3J = 7.0 Hz), 1.21 (t)
		m	dq	dq	ddq	ddtd	dt	dd dd s	
trans-**10c**	OCH_2CF_3	3.12	5.58	5.85	2.76	2.45	4.18	4.05, 4.26, 3.03	3.85 (q, $J_{H,F}$ = 8.7 Hz)
trans-**11**	OSO_2CH_3	ca. 3.32	5.63	5.88	2.95	2.67	5.18	4.15, 4.35, 3.03	3.06

[a] The assignments are based on NOE measurements.

ethers *cis*-**10b** and *trans*-**10b**, as well as a 3:1 mixture of the dimesylates *cis*-**11** and *trans*-**11**, in yields of 45, 4 and 7%, respectively. The solvolysis in TFE afforded a 4:1:1 mixture of the trifluoroethyl ethers *cis*-**10c** and *trans*-**10c** and the dimesylate *cis*-**11**, from which pure *cis*-**10c** was isolated in 13% yield.

The structure of the products was determined from their analytical and spectral data. Even though we did not try to obtain elemental analyses or high resolution mass spectra of the *trans* products, there is no doubt as to the identity of these compounds, due on one hand to the close similarities of their NMR spectra to those of the corresponding *cis* isomers and on the other hand to certain characteristic differences between them. The assignment of configuration is based on the magnitude of the mutual coupling of the protons in positions 1 and 5 ($J_{1,5}$) and on the effects of the 5-substituents on the ^{13}C NMR chemical shifts of the mesyloxymethyl group. Cyclopentene and its simple derivatives are nearly planar. Thus, larger values of $J_{1,5}$ are to be expected for *cis*-**10a**, *cis*-**10b**, *cis*-**10c** and *cis*-**11** than for their *trans* isomers, on the basis of the Karplus-Conroy relationship. Therefore, the compounds exhibiting values of 6.2−7.0 Hz were assigned to the *cis* series and those with values of 3.4−3.5 Hz to the *trans* series (Table 1). A *cis*-vicinal orientation of two substituents of a ring compound (as opposed to a *trans*-vicinal orientation) produces characteristic high-field absorptions in the ^{13}C NMR spectrum of the respective carbon atoms directly bound to the ring (γ *gauche* or *syn* effects[13a]). In the spectra of the diastereomeric pairs of **10a**, **10b**, **10c** and **11**, the CH_2 signal of the mesyloxymethyl groups of the major product is consistently found at higher field (by 0.7−1.6 ppm, Table 2), and so, in line with the criterion based on the interproton coupling constant $J_{1,5}$, the *cis* configuration has been ascribed to this isomer.

In addition to the spectroscopic evidence, the *cis* configuration in the substrate (*cis*-**10a**) and the *cis* annulation of the product (**12**, Scheme 5) are supported by the conversion of the major product formed on hydrolysis of *endo,endo*-**9** into an oxetane derivative. It is considered unlikely that such a ring-closure would proceed so readily in the case of *trans*-**10a**.



Scheme 5. Supporting chemical evidence for the stereochemical assignment of *cis*-**10**a

Rates of solvolyses of *endo,endo*-**9** were investigated in sufficient detail (Table 3) to allow comparisons with rates of reactions of other substrates at different temperatures and/or in different solvents.

3. Synthesis of the Dimesylate *exo,exo*-9

In order to test the mechanistic proposal for the solvolysis of *endo,endo*-**9** (see below), we reasoned that the study of a diastereomer of *endo,endo*-**9** might be conclusive. In particular, the independent generation of the cation *eq*-**31** was expected to yield the products of the *trans* series (*trans*-**10**, *trans*-**11**) exclusively. To that end, we synthesised *exo,exo*-**9**; in view of the same product **7** reported for the solvolysis of *endo*-**6** and *exo*-**6**[4] (Scheme 2), this substrate appeared to be the perfect precursor to *eq*-**31**. Snyder and Dougherty [14] had already prepared the bis(*tert*-butyldimethylsilyl ether) **15a** of *exo,exo*-**8** (Scheme 6). Thus, we expected that the preparation of *exo,exo*-**9** would be straightforward. As in the case of *endo,endo*-**9**, the starting material was benzvalene,[7] to which elemental bromine was added to give *endo*-5,*anti*-6-dibromobicyclo[2.1.1]hex-2-ene.[15] Ozonolysis of this dibromide and reduction of the ozonide produced the dibromocyclobutanedimethanol **13**, which was converted into the bicyclobutane derivative **15a** via the bis(silyl ether) **14a** of **13**.[14]

The next step would have been the deprotection of **15a**. However, we were unable to observe any *exo,exo*-**8** under the various conditions to which **15a** was subjected according to literature procedures ($Bu_4N^+F^-$ in THF, $H_4N^+F^-$ in CH_3OH, DIBAL-H in CH_2Cl_2, basic Al_2O_3 of activity II in hexane). Therefore, we had to restart from **13**, prepar-

Table 2. ^{13}C NMR chemical shifts of 5-substituted cyclopent-2-ene-1-methanol mesylates in $CDCl_3$, δ values [$\delta(CDCl_3) = 77.0$]

Compd.	5-Subst.	C-1	C-2	C-3	C-4	C-5	$CH_2OSO_2CH_3$	Signals of the 5-subst.
cis-**10a**[a]	OH	49.6	127.7	131.3	42.2	71.4	68.7, 37.1	–
cis-**10b**[a]	OC_2H_5	47.6	128.9	131.1	38.2	79.0	69.6, 37.0	15.3, 65.3
cis-**10c**	OCH_2CF_3	48.2	128.3	130.6	38.1	81.1	68.4, 36.9	67.4 ($J_{C,F}$ = 34 Hz), 123.8 ($J_{C,F}$ = 279 Hz)
cis-**11**[a]	OSO_2CH_3	48.2	127.4	130.7	39.8	79.7	66.9, 37.3	38.2
trans-**10a**	OH	54.7	127.3	131.9	41.7	74.4	70.1, 37.6	–
trans-**10b**[a]	OC_2H_5	52.0	127.5	131.9	38.9	80.9	70.3, 37.4	15.3, 64.4
trans-**10c**	OCH_2CF_3	52.1	127.1	131.6	38.6	83.1	69.4, 37.5	[b]
trans-**11**[a]	OSO_2CH_3	52.5	127.0	131.1	39.5	81.7	68.5, 37.4	38.3

[a] The assignments are based on a C,H COSY spectrum. – [b] Not observed due to low intensity.

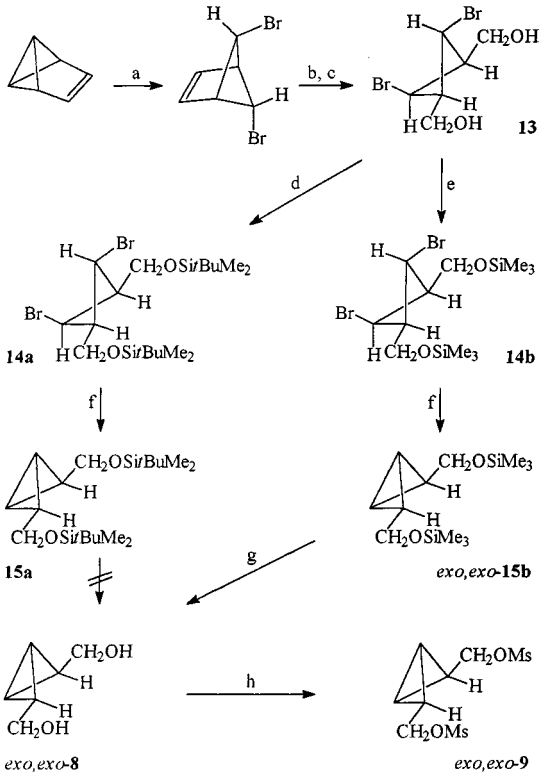
Table 3. Rate constants k for solvolyses of the dimesylate *endo*,*endo*-**9** in ethanol (EtOH), 80% and 60% v/v ethanol/water (80% EtOH, 60% EtOH), 60% and 40% v/v acetone/water (60% A, 40% A) and 97% w/w 2,2,2-trifluoroethanol/water (97% TFE)

Solvent	T [°C]	k [s^{-1}][a]	Y_{OMs}[b]
EtOH	60.0	$(3.38 \pm 0.03) \times 10^{-4}$	
	40.0	$(4.90 \pm 0.1) \times 10^{-5}$[c][d]	
	25.0	9.7×10^{-6}[e]	−2.22
80% EtOH	25.0	$(6.92 \pm 0.21) \times 10^{-5}$	0.00
60% EtOH	25.0	$(1.63 \pm 0.21) \times 10^{-4}$	1.13
	25.0	$(1.93 \pm 0.08) \times 10^{-4}$[f]	
60% A	40.0	$(4.27 \pm 0.18) \times 10^{-4}$[g]	
	25.0	$(8.2 \pm 0.5) \times 10^{-5}$ [c][h]	0.66
40% A	25.0	$(3.24 \pm 0.10) \times 10^{-4}$	1.94
97% TFE	25.0	$(2.00 \pm 0.06) \times 10^{-4}$	1.92

[a] Determined conductimetrically in triplicate, except where stated otherwise; errors shown are average deviations. – [b] Data from ref.[3] – [c] Duplicate measurements of rate constant. – [d] $\Delta H^{\neq}$ = 19.4 kcal mol^{-1}, $\Delta S^{\neq}$ = −16.5 cal mol^{-1} K^{-1}. – [e] Calculated from rate data at higher temperatures. – [f] In the presence of four equivalents of triethylamine. – [g] Quadruplicate measurements of rate constant. – [h] $\Delta H^{\neq}$ = 19.8 kcal mol^{-1}, $\Delta S^{\neq}$ = −10.8 cal mol^{-1} K^{-1}.

ing its bis(trimethylsilyl ether) **14b** and cyclising this with *tert*-butyllithium. The resulting bicyclobutane derivative *exo*,*exo*-**15b** was readily transformed into *exo*,*exo*-**8** by potassium carbonate in methanol and the final step, the double mesylation of *exo*,*exo*-**8** with formation of *exo*,*exo*-**9**, was achieved under routine conditions.

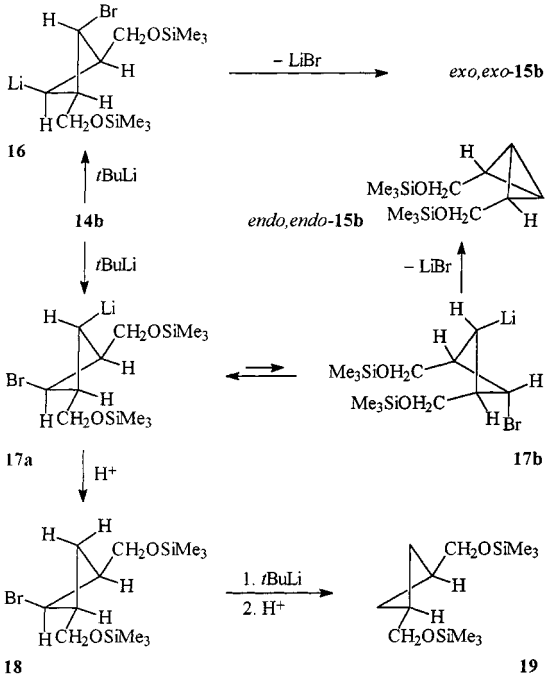
This reaction sequence did not proceed as smoothly as depicted in Scheme 6, however. Snyder and Dougherty[14] note that the conversion of **14a** into **15a** is accompanied by the production of a small amount of the *endo*,*endo* isomer of **15a**. We were not looking carefully for *endo*,*endo*-**15b** (Scheme 7), but its presence was later proven by the observation of *endo*,*endo*-**8** and *endo*,*endo*-**9** as admixtures with *exo*,*exo*-**8** and *exo*,*exo*-**9**, respectively. The dimesylate *endo*,*endo*-**9** was not the only impurity in *exo*,*exo*-**9**. For the solvolysis (see Section 4), we employed a 36:1:16 mixture of *exo*,*exo*-**9**, *endo*,*endo*-**9** and *cis*-cyclobutane-1,3-dimethanol dimesylate (**23**, Scheme 8). This clearly indicates that *exo*,*exo*-**15b** and *exo*,*exo*-**8** must also have been contaminated with the bis(trimethylsilyl ether) **19** (Scheme 7) and the dialcohol **22** (Scheme 8), respectively. However, we did not identify the side products of every step in the first successful execution of the synthesis of *exo*,*exo*-**9**. On the other



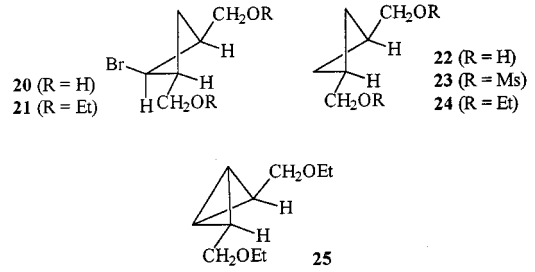
Scheme 6. Synthesis of *exo*,*exo*-**9**: a) Br_2, Et_2O/CCl_4, 0 °C; b) O_3, CCl_4/CH_2Cl_2, −78 °C; c) $LiAlH_4$, Et_2O, reflux; then H_2O; d) *t*BuMe_2SiCl, imidazole; e) Me_3SiCl, NEt_3; f) *t*BuLi, Et_2O, −78 °C; g) K_2CO_3, MeOH; h) $MeSO_2Cl$, NEt_3, −30 to 0 °C

hand, several repetitions of the treatment of **14b** with *tert*-butyllithium furnished as a major side product the bromine derivative **18** instead of **19** and, in consequence, *exo*,*exo*-**8** was obtained as a mixture with the bromodialcohol **20** (Scheme 8). These variations, as well as substantial fluctuations in the product ratios, characterised the rather capricious ring-closure of **14b**. Since attempts to purify *exo*,*exo*-**15b**, *exo*,*exo*-**8** and *exo*,*exo*-**9** were unsuccessful, the solvolyses of *exo*,*exo*-**9** had to be carried out in the presence of admixtures.

Although we did not determine the configurations of **18** and **20**, we assume that the bromine atom is located *cis* to the other substituents. This is based on the mechanistic model for the reaction between **14b** and *tert*-butyllithium, illustrated in Scheme 7. The reason for the formation of sev-



Scheme 7. Proposed mechanism for the reaction between **14b** and *tert*-butyllithium



Scheme 8. Side products from the preparation of *exo,exo*-**8** and *exo,exo*-**9**, and model compounds for the products of the solvolyses of *exo,exo*-**9** and the ditosylate **28**

eral products seems to be the occurrence of bromine−lithium exchange at two different sites, resulting in the two isomeric lithium compounds **16** and **17**. While **16** should rapidly undergo the elimination of lithium bromide and give rise to *exo,exo*-**15b**, if the C−C bond formation proceeds by rear-side attack (S_N2 type) of the carbanionic centre at the bromine-bearing carbon atom, **17a** may be unable to transform into *exo,exo*-**15b** due to the unsuitable configuration of the electrophilic centre. This obstacle is removed by the conformational conversion of the four-membered ring, furnishing **17b**, which should be the precursor to *endo,endo*-**15b**. However, **17b** carries its two large substituents in *syn-pseudoaxial* positions and thus is less stable than **17a**; apparently only **17a** is capable of abstracting a proton from the solvent (diethyl ether) or from the rather acidic bridgehead CH groups of *exo,exo*-**15b** already present with formation of **18**. Furthermore, **18** should on its part be amenable to the bromine−lithium exchange and a proton abstraction by the resulting lithium compound would explain the appearance of **19**.

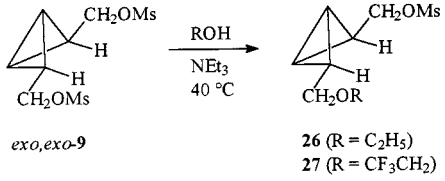
In order to compare them with the ethanolysis products of *exo,exo*-**9** and the ditosylate **28**, we prepared the diethyl ethers **24** and **25** (Scheme 8), employing a standard procedure, i.e., treatment of the dialcohols with sodium hydride in the presence of iodoethane. In the case of **25**, a sample of *exo,exo*-**8** containing **20** was used; this gave a mixture of **21** and **25**.

Structural assignments of all new compounds were based on known NMR parameters of model compounds, namely those of **15a**[14] for the bicyclobutane derivatives (*exo,exo*-**8**, *exo,exo*-**9**, *exo,exo*-**15b**, **25**), those of **22**[6] for the disubstituted cyclobutanes (**23**, **24**), and those of (1α,2α,3α)-2-(phenylsulfanyl)cyclobutane-1,3-dimethanol[6] for the trisubstituted cyclobutanes (**18**, **20**, **21**). The parent bicyclobutane shows highly characteristic one-bond $^{13}C,H$ coupling constants.[13b] The respective values of 203, 210 and 204 Hz for the signals at δ = 3.2, 5.2 and 4.0 (C-1) and those of 166, 173 and 168 Hz for the signals at δ = 42.8, 37.7 and 40.4 (C-2) clearly establish the bicyclobutane nature of *exo,exo*-**8** and *exo,exo*-**9**, as well as **25**.

4. Solvolyses of the Dimesylate *exo,exo*-9 and the Ditosylate 28

Because of the lack of pure *exo,exo*-**9**, we investigated a 36:1:16 mixture of the three dimesylates *exo,exo*-**9**, *endo,endo*-**9** and **23**. Whereas the proportion of *endo,endo*-**9** was so small that its products (**10**, **11**) did not interfere with the analysis of the products from *exo,exo*-**9**, virtually none of **23** was consumed under the reaction conditions (cf. the rate ratio for the solvolyses of *exo,exo*-**9** and the ditosylate **28** in Table 4).

Warming of the above mixture in 60% aqueous acetone in the presence of triethylamine at 40 °C over five days resulted in a decrease of 75% in the proportion of *exo,exo*-**9**, but no product could be identified. When anhydrous ethanol, containing triethylamine, was used as solvent, a new product was observed. Within three and seven days, respectively, at 40 °C, the proportion of *exo,exo*-**9** had decreased by 30 and 50% and a new compound was present in yields of approximately 70 and 50% (based on starting material consumed). Since attempts to isolate it were to no avail, we resorted to a detailed analysis of the NMR spectra of the crude product. The ^{13}C NMR signals at δ = 4.7, 38.0 and 40.2, with an intensity ratio of 2:1:1 and one-bond $^{13}C,H$ coupling constants of 207, 173 and 169 Hz, respectively, characterised it as an unsymmetrical bicyclobutane derivative. Comparing all the data with those of *exo,exo*-**9** and the bis(ethyl ether) **25**, we propose structure **26** for the ethanolysis product (Scheme 9). The analogous compound **27** was formed when 2,2,2-trifluoroethanol was used as solvent.

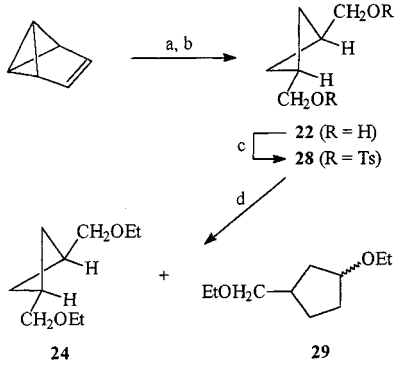


Scheme 9. Products of the solvolyses of *exo,exo*-**9**

Apart from **26** and **27**, no further products could be discerned. We suspect that **26** and **27** solvolysed on their part to give the bis(ethyl ether) **25** and its hexafluoro derivative, respectively, but these compounds would not have survived under the reaction conditions. In a control experiment, we treated **25**, dissolved in ethanol, with the triethylamine/triethylammonium mesylate buffer that developed during the ethanolysis of *exo*,*exo*-**9** and after one hour at 20 °C were no longer able to observe any **25**. Most probably, the mixture was acidic enough to cause the acid-catalysed addition of ethanol to **25**. Reactions of this type are well known for many bicyclobutane derivatives.[16]

Rates of solvolyses of *exo*,*exo*-**9** were investigated conductimetrically in 40% v/v acetone/water (40% A) at 25, 40 and 60 °C and in 97% w/w trifluoroethanol/water (97% TFE) at 40 °C, with and without added lutidine. Unfortunately, however, accurate values were not obtained. The rate constant in 40% A at 25 °C was approximately 4×10^{-5} s^{-1}, and the values were similar whether in the presence or in the absence of the buffer. Rate constants in 40% A and 97% TFE at 40 °C were very similar (ca. 2×10^{-4} s^{-1}).

The most stable conformers of the *cis*-1,3-disubstituted cyclobutanes **19** and **22**−**24** bear their substituents in *pseudoequatorial* positions. Therefore, the shape of these molecules resembles that of *exo*,*exo*-**9** rather closely. Thus, on the basis of kinetic studies of solvolyses of cyclobutanemethanol sulfonates,[17,18] the dimesylate **23** is considered to be an appropriate model with which to estimate the effect of one mesylate group of *exo*,*exo*-**9** on the solvolysis rate of the other. Since mesylates and tosylates solvolyse approximately equally rapidly,[3] we chose to study the ditosylate **28**. Of the known routes to this compound,[19−21] its synthesis from benzvalene (Scheme 10)[6,21] proved to be the most convenient one for us.



24 29

Scheme 10. Synthesis and ethanolysis of the ditosylate **28**: a) O_3, Et_2O, −78 °C; b) $LiAlH_4$, Et_2O/THF, reflux; then H_2O; c) 4-$MeC_6H_4SO_2Cl$, pyridine; d) EtOH, 80 °C

When heated at 80 °C in anhydrous ethanol in the presence of triethylamine, **28** was consumed completely within seven days and gave a mixture of rather volatile products, probably as the result of elimination reactions. In consequence, we repeated the experiment in the absence of the base, and obtained an 18% yield of a mixture of three bis(ethyl ethers), shown by GC-MS to be isomers, present in the ratio of 10:1:7. The major component was identified as the nonrearranged bis(ethyl ether) **24**, as corroborated by an independent synthesis from **22** with sodium hydride and iodoethane. Because of their very similar mass spectra (also with respect to the intensities of the signals), we propose that the two further products were stereoisomers. The NMR spectra of the more abundant one are in line with the structure of a cyclopentane derivative **29**.

Although ditosylate **28** is only sparingly soluble in aqueous media, a satisfactory rate constant could be obtained through our usual conductimetric procedure of injecting μL quantities of a 1% acetonitrile solution of **28** into mL quantities of the preprepared bulk solvolysis medium. Better results were obtained when a 10^{-4} M solution in 40% A was prepared by first dissolving **28** in mL quantities of pure acetone prior to preparing the bulk solvolysis medium. As determined from the mean of four measurements, the rate constant in 40% A at 75 °C was $(8.0 \pm 0.2) \times 10^{-5}$ s^{-1}.

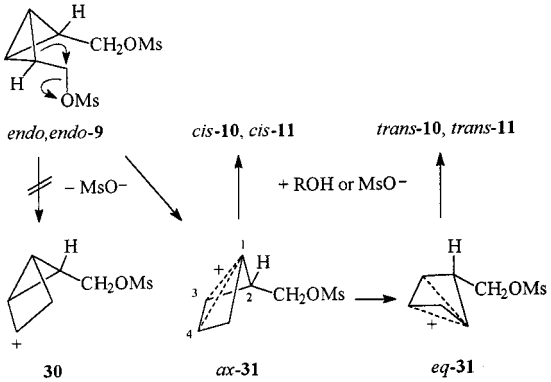
Discussion

1. Product Studies

In view of the common product **7** described as arising from the solvolyses of *endo*-**6** and *exo*-**6**,[4] the different constitution of the products resulting from the reactions of *endo*,*endo*-**9** and *exo*,*exo*-**9** − i.e., **10** and **11** from the former and **26** and **27** from the latter − were extremely surprising. Since the behaviour of *endo*,*endo*-**9** is closely related to that of the cyclic bicyclobut-2-ylcarbinyl esters **1**−**3**, we start the discussion with this substrate.

As only rearranged products were found, it is highly unlikely that a bicyclobut-2-ylcarbinyl cation was formed during the solvolyses of *endo*,*endo*-**9**. The dissociation was accompanied by a Wagner−Meerwein rearrangement, resulting in a ring-expansion, but there is no evidence for the formation of the cyclobutyl cation **30** (Scheme 11), since none of the products possesses a bicyclo[2.1.0]pentane skeleton substituted in the 2-position. Ab initio MO calculations show that the corresponding parent cation (in which H replaces CH_2OMs) is not a minimum on the potential energy surface of the C_5H_7 cations and the favoured intermediate is the nonclassical cyclopent-3-en-1-yl cation.[22,23] Stereochemical studies,[24,25] as well as the calculations mentioned,[22,23] support the bishomoaromatic nature of this species, which is a bishomocyclopropenyl cation.[26] Its 1,3-dimethyl derivative should be generated from *endo*-**6** and trapped by water to give **7**. Accordingly, the solvolysis of *endo*,*endo*-**9** should initially produce the cation *ax*-**31**, a *pseudoaxial* 2-methanesulfonyloxymethyl-substituted derivative of the nonclassical cyclopent-3-en-1-yl cation. Previously, it had convincingly been shown that nucleophiles attack such cations at C-1, from the side opposite to the two-electron, three-centre bond.[24,25] Applied to *ax*-**31**, this principle explains the formation of the products *cis*-**10** and *cis*-**11**, with *cis*-**11** resulting from internal return of the initially generated ion pair consisting of *ax*-**31** and the mesylate ion. So far, the solvolysis of *endo*,*endo*-**9** is entirely ana-

logous to that of the bridged bicyclobutylcarbinyl sulfonates **1**−**3**.



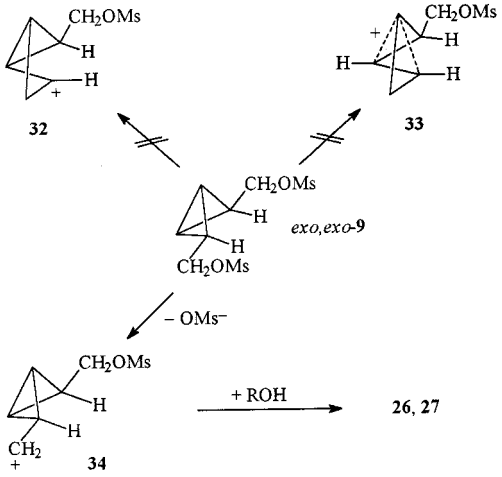
Scheme 11. Proposed mechanism for the solvolyses of *endo*,*endo*-**9**

But which pathway gives rise to *trans*-**10** and *trans*-**11**? Two possibilities are obvious: (i) the isomerisation of *ax*-**31** to its diastereomer *eq*-**31** and addition of the nucleophiles to the latter, and (ii) the S_N2 reaction of *cis*-**11**, observed in all cases, with the nucleophiles of the mixtures. The latter alternative was ruled out with the aid of a control experiment, in which pure *cis*-dimesylate *cis*-**11** was found to be entirely unchanged on exposure to the conditions used for the ethanolysis of *endo*,*endo*-**9**.

Thus, our results support, for the first time, the ability of a nonclassical cyclopent-3-en-1-yl cation to undergo a change in configuration. As deuterated derivatives of the parent cation do not show this mobility,[24,25] the reason for a rather low barrier to the conversion of *ax*-**31** into *eq*-**31** may be the steric interaction of the CH_2OMs group with the coaxial hydrogen atom at the 5-position. Being similar to one *gauche* interaction of an *axial* methyl group in cyclohexane (0.9 kcal mol^{-1} [27]), this effect should raise the energy of *ax*-**31** relative to that of the parent cation. However, this effect should be greatly reduced in the transition state en route to *eq*-**31** and absent in *eq*-**31** itself, since there the CH_2OMs group occupies a *pseudoequatorial* position. In consequence, a lower activation energy is expected for the configurational conversion of *ax*-**31**, compared to the parent cation. As transition state for this conversion, the respective classical cyclopent-3-en-1-yl cation is required.[22,23] The corresponding unsubstituted species has been calculated to be less stable than the nonclassical isomer by 6 kcal mol^{-1} (4.5 kcal mol^{-1} after correction for the zero-point energy) in the gas phase.[23] Solvation may reduce this energy difference somewhat, which is in line with our assumption of competition between the interception of *ax*-**31** by nucleophiles and its conversion into *eq*-**31**.

Direct access to the cation *eq*-**31** would allow an examination of our proposal that *eq*-**31** has a higher barrier to conversion into *ax*-**31** than vice versa. Since *ax*-**31** produces only a small amount of *trans* products (*trans*-**10**, *trans*-**11**), formed through *eq*-**31**, products of that type should be formed exclusively from *eq*-**31**. Relying on the findings documented for the solvolysis of *endo*-**6** and *exo*-**6**, in particular the formation of the same product **7,** but also on the greater rate constant for *exo*-**6**,[4] we anticipated that the dimesylate *exo*,*exo*-**9** would be a very suitable substrate. However, the outcome of the solvolyses of *exo*,*exo*-**9** is entirely at variance with the previous results.[4]

The formation of the bicyclobutane derivatives **26** and **27** can be explained either by an S_N2 reaction or by an S_N1 process without rearrangement. We favour the latter possibility on the basis of the rather mild reaction conditions, the absence of any strong nucleophile that might have triggered the bimolecular substitution and on the low sensitivity of the solvolysis rate to a change in solvent nucleophilicity (similar rate constants in 40% A and 97% TFE[3]). The S_N1 pathway raises the urgent questions of why the heterolytic dissociation of *exo*,*exo*-**9** would proceed without neighbouring group participation and why the bicyclobut-2-yl cation **34** would not rearrange (Scheme 12).



Scheme 12. Proposed mechanism for the solvolyses of *exo*,*exo*-**9**

Contrary to our initial expectations, a detailed analysis reveals that no pathway as smooth as the step from *endo*,*endo*-**9** to *ax*-**31** is accessible to *exo*,*exo*-**9**. According to the Woodward−Hoffmann rules,[28] the Wagner−Meerwein rearrangement follows a suprafacial-suprafacial course. Thus, if **34** expanded one ring or if *exo*,*exo*-**9** dissociated with neighbouring-group participation, either the classical cation **32** or the nonclassical one **33** would result; both of these would be very unfavourable. Apart from the orientation of the substituent, **32** is a highly strained conformation of **30**. The conformational conversion of **32** would occur through a transition state similar to a classical cyclobutyl cation, without any stabilisation. Since quantum-chemical calculations have shown that the planar cyclobutyl cation is not an energy minimum[29] and that classical cyclobutyl cations only exist when there is massive electronic stabilisation (such as by a phenyl group[30]), the pathway through **32** involves a high energy barrier. The step from *exo*,*exo*-**9** to **33** corresponds exactly to the generation of *ax*-**31** from *endo*,*endo*-**9**. Whereas a CH group (C-1) bridges a *cis*-but-2-ene subunit in *ax*-**31** (and *eq*-**31**), it is necessary to span a *trans*-but-2-ene moiety in **33**. Since the respective termini (C-2 and C-5) are much farther apart in **33** than in *ax*-**31**, a prohibitive strain would build up in **33**. On the other hand, the direct conversion of *exo*,*exo*-**9** or

the rearrangement of **34** into the mirror image of *eq*-**31** would be a suprafacial-antarafacial process, forbidden by the Woodward−Hoffmann rules.

As expected on the basis of the acetolysis of cyclobutanemethanol tosylate, the ethanolysis of the ditosylate **28** proceeded rather slowly. In the former case, the isolated product consisted of 99% cyclopentyl acetate and only 1% cyclobutanemethanol acetate.[17] A substantially greater proportion of **28** underwent ethanolysis without ring-expansion to give **24**, from which two consecutive S_N2 reactions were indicated. This was interpreted in terms of the destabilising effect exerted by the oxygen-containing functionality on the cation that has to be involved en route to the rearranged products **29**.

2. Kinetic Studies

Since rates of solvolyses of tosylates and mesylates are very similar (usually tosylates react slightly more rapidly[3]), we compared the data for *endo*,*endo*-**9** (Table 3) with those for the less flexible ditosylate **2**.[1] Solvolyses of *endo*,*endo*-**9** were about 5 times faster in 80% EtOH (5.3 times faster), 60% A (4.7 times faster), and 97% TFE (5.2 times faster). The rate constants showed only a weak response to changes in solvent nucleophilicity, as demonstrated by the similar values for reactions in 40% A and 97% TFE, solvents of similar ionising power but different nucleophilicities.[3] A low response (*m*) to changes in solvent ionising power is expected for a delocalised transition state arising from σ-participation (Scheme 11). Calculated from the slopes of a plot of logarithms of rate constants versus Y_{OMs} (values given in Table 3), *m* is 0.33 ± 0.03 for *endo*,*endo*-**9** (six solvents) compared with 0.53 ± 0.12 for **2** (three solvents) and with 1.00 (by definition) for solvolyses of 1-adamantyl mesylate.[3]

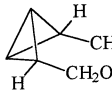
About 8-fold slower than those of *endo*,*endo*-**9**, rates of solvolyses of the dimesylate *exo*,*exo*-**9** can be explained by weaker σ-participation; a counter-effect is the closer proximity of the two sulfonate groups in *endo*,*endo*-**9**, which would be expected to retard its rate.[1] Remarkably, it does not make a big difference whether or not the bicyclobutane system is rearranging. In other words, the cations formed (*ax*-**31** and **34**) should be similar in energy. This is not too surprising, as the calculations mentioned above[29] showed that the cyclopropylcarbinyl cation and its ring-expansion product − the bicyclobutonium ion − had almost identical energies.

Comparing solvolyses of monotosylates *exo*-**6** and *endo*-**6**,[4] in which there cannot be any rate-retarding effects from adjacent sulfonate groups, *exo*-**6** was reported to react slightly more rapidly (2-fold) than *endo*-**6** in 80% dioxane/water ($Y_{OTs} = -1.3$[3]) at 25 °C. The rate constant calculated for the solvolysis of *endo*-**6** in 80% EtOH at 25 °C (assuming $m = 0.5$) was 1.2×10^{-3} s^{-1}, surprisingly only 17-fold faster than the value of 6.9×10^{-5} s^{-1} (Table 3) for *endo*,*endo*-**9**, despite **6** having the advantages of (i) the presence of two methyl groups, each enhancing the rate at least 5-fold, as observed in solvolyses of cyclopropylcarbinyl esters,[31] and (ii) the lack of the second sulfonate group, retarding the rate by factors of about 10^3 for groups in close proximity.[1]

Solvolyses of cyclobutylcarbinyl sulfonates are thought to occur with moderate σ-participation[32] and are relatively insensitive to solvent nucleophilicity; there is a linear correlation of rates of solvolyses of cyclobutylcarbinyl brosylate (*p*-bromobenzenesulfonate) with those of neophyl tosylate, for example.[33] Cyclobutylcarbinyl brosylate solvolysed in 40% EtOH at 45 °C with a rate constant of 6.5×10^{-4} s^{-1},[18] and the ditosylate **28** solvolysed in 40% A at 75 °C with a rate constant of 8.0×10^{-5} s^{-1} (see above). If the corrections for leaving group (a brosylate/tosylate ratio of 5 can be assumed[34a]) and temperature (about 15-fold) are combined, ignoring the minor difference in solvents, it can be estimated that the ditosylate **28** is about 25-fold less reactive than cyclobutylcarbinyl tosylate. After loss of the first OTs group in the ethanolysis of **28**, leading to direct substitution, a CH_2OEt group replaces one of the CH_2OTs groups. The σ_I value of 0.3 for OMe/OEt is about half of that of OTs ($\sigma_I = 0.58$),[34b] so a greater rate-retarding effect, of about 5-fold, is to be expected for the first ionisation step relative to the second one. Consequently, the deactivating effect of a CH_2OTs group relative to a CH_2OEt group explains why loss of the second tosylate group is faster than that of the first one, and so the isolated nonrearranged product of ethanolysis of **28** is the bis(ether) **24**.

The rate-retarding effect of one sulfonate group on the reactivity of an adjacent sulfonate group is similarly one of the factors to be considered when rearrangement occurs, but the change in the carbon skeleton is also important. Solvolyses of cyclopentylcarbinyl brosylate are significantly slower than solvolyses of cyclobutylcarbinyl brosylate, by over 40-fold in 40% EtOH.[18] Hence, rearrangement probably occurs when the second tosylate group is lost during the ethanolysis of **28** to **29**. In contrast, solvolysis of *endo*,*endo*-**9** results in the deactivated cyclopentenylcarbinyl system **10**, so the loss of the first mesylate group occurs more rapidly than that of the second, and monomesylates are isolated (Scheme 4).

Returning again to the solvolyses of **6**, the reported rate constants[4] are orders of magnitude (10^2 or 10^3) slower than those to be expected from the arguments outlined above. The presence of an additional strongly electron-withdrawing sulfonate group in **9** may stabilise the bicyclobutane skeleton, and the instability of the ether **25** (see Exp. Sect.) demonstrates how fragile **6** might be. These kinetic arguments support our other doubts (see above) about the published data for solvolyses of **6**.[4]



35

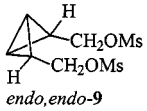
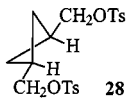
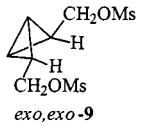
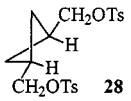
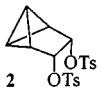
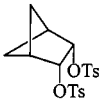
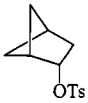
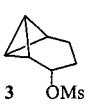
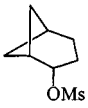
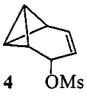
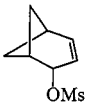
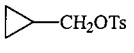
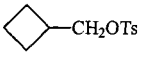
There are two equivalent ways in which we can obtain an estimate of the reactivity of the nonbridged bicyclobut-2-ylcarbinyl tosylate **35**, which is a model for *endo*-**6** and rather closely related to *endo*,*endo*-**9** as well. Firstly, a rate factor of 3×10^3 (based on solvolyses of **1** and **2**) may be

applied for the rate-retarding effect of the extra sulfonate group on *endo*,*endo*-**9**, or secondly, it may be assumed that **35** reacts 5 times more rapidly than the corresponding bridged compound **1**, as observed for *endo*,*endo*-**9** compared with **2**. This produces an estimate of 0.2 s^{-1} (very similar to that for **3**) for the solvolysis of **35** in 80% EtOH at 25 °C. The corresponding value for cyclopropylcarbinyl mesylate is 2.49 × 10^{-3} s^{-1},[2] so **35** is calculated to react 80 times more rapidly, due in part to the presence of two additional carbon atoms. However, the reliability of the estimate of 0.2 s^{-1} depends heavily on the assumed rate-retarding effect of the second sulfonate group. A factor of at least 10^3 for two mesylate or tosylate groups in close proximity applies to **2** versus **1**, and the corresponding bicyclo[2.1.1]hexyl[1] and *cis*-1,2-cyclohexyl substrates,[35] but the effect in *endo*,*endo*-**9** may be lower.

Comparisons of the reactivities of bicyclobutylcarbinyl and corresponding cyclobutylcarbinyl substrates show wide variations (Table 4). The two values greater than 10^5 were noted earlier[1] as similar to those expected for solvolyses of cyclopropylcarbinyl esters, but later results (Table 4) showed a wide range of other values, down to as low as 12. The parent cyclopropylcarbinyl and cyclobutylcarbinyl tosylates gave a ratio of 2 × 10^3 in EtOH (Table 4), although this ratio will vary with solvent ionising power and solvent nucleophilicity.[36]

The greater distance (through space, not through bonds) between the two sulfonate groups is probably the main factor accounting for the relatively high reactivity of **28**, which reacts only 6 × 10^2 times more slowly than *endo*,*endo*-**9** under comparable conditions (Table 4). For reasons discussed above, *exo*,*exo*-**9** reacts relatively slowly. Solvolysis of the bicyclo[3.1.1]heptyl mesylate is strongly enhanced by σ-participation, resulting in rearrangement,[37] and it reacts only 12-fold more slowly than the tricyclic analogue. Conversely, the high ratios (10^5) in Table 4 may reflect smaller contributions to the rate enhancements due to the cyclobutylcarbinyl unit in the bicyclo[2.1.1]hexyl substrates.

Table 4. Ratios of rate constants for solvolyses of bicyclo[1.1.0]but-2-ylcarbinyl sulfonates or cyclopropylcarbinyl tosylate and the corresponding cyclobutylcarbinyl sulfonates

bicyclobutylcarbinyl, cyclopropylcarbinyl	cyclobutylcarbinyl	ratio	conditions, source
 *endo,endo*-**9**	 **28**	6 × 10^2	[a,b]
 *exo,exo*-**9**	 **28**	50	[b,c]
 **2**		6 × 10^5	[d]
 **1**		1.4 × 10^5	[d]
 **3**		12	[e]
 **4**		2 × 10^3	[f]
		2 × 10^3	[g]

[a] In 40% A at 75 °C; the rate constant for *endo*,*endo*-**9** (Table 3) in 40% A at 25 °C was multiplied by 130 to correct to 75 °C and by 1.1[3] to correct for the change in leaving group. – [b] See Results, Section 4 for the rate constant of **28**. – [c] In 40% A at 75 °C; rate constants for *exo*,*exo*-**9** (see Results, Section 4) at 25, 40, and 60 °C were extrapolated to 75 °C to give a value of ca. 4 × 10^{-3} s^{-1}. – [d] In 80% EtOH at 25 °C; rate constants from Table 6 of ref.[1] – [e] In 80% EtOH at 25 °C; rate constants from Table 1 of ref.[2] and Table 5 of ref.[37] – [f] In EtOH at 25 °C; rate constants from Table 1 of ref.[2] – [g] In EtOH at 45 °C; rate constants for cyclopropylcarbinyl tosylate at 20, 30, and 40 °C[38] were extrapolated to 45 °C and the rate constant for cyclobutylcarbinyl brosylate[39] was divided by 5.[34a]

Conclusion

It is proposed that the solvolyses of the title dimesylate *endo*,*endo*-**9**, affording the 5-substituted cyclopent-2-ene-1-methanol mesylates **10** and **11**, proceed through a cation of the cyclopent-3-en-1-yl type (*ax*-**31**) and thus are believed to present a new means of access to this bishomoaromatic system. A CH_2OMs substituent in the 2-*pseudoaxial* position, serving as a stereochemical label, indicates the rather easy conversion of *ax*-**31** into a second cation of the same kind, but bearing the substituent in the 2-*pseudoequatorial* position (*eq*-**31**). This mobility had not been observed previously, but is in agreement with quantum-chemical calculations, which ascribe an energy enhanced by only 6 kcal mol^{-1} to the planar cyclopent-3-en-1-yl cation relative to the bishomoaromatic state.[23] The respective classical cation is assumed to be the transition state between *ax*-**31** and *eq*-**31**. Unexpectedly, the second title dimesylate *exo*,*exo*-**9** exhibited entirely different behaviour, as its solvolyses gave rise exclusively to nonrearranged products (**26**, **27**), which, for the first time, offered strong evidence for the intermediacy of a bicyclo[1.1.0]but-2-*exo*-ylcarbinyl cation (**34**). The different results for the reactions of the stereoisomeric substrates **9** are explicable in terms of the suprafacial-suprafacial course of the Wagner–Meerwein rearrangement. Thus, heterolytic dissociation of *endo*,*endo*-**9** and simultaneous rearrangement generate the favourable cation *ax*-**31**, whereas in the case of *exo*,*exo*-**9** the same sequence would lead to a highly strained species such as **33**. To avoid a high-energy intermediate, solvolyses of *exo*,*exo*-**9** occur without rearrangement, most probably through the cation **34**, which is a viable alternative due to its cyclopropylcarbinyl nature.

Since the above findings are at variance with the product **7** reported for the solvolysis of the tosylate *exo*-**6**,[4] which is reported to solvolyse surprisingly slowly, we suspect that the highly sensitive bicyclobutane derivative reacted before solvolysis occurred.

Comparisons of kinetic data for solvolyses of bicyclobut-2-ylcarbinyl and cyclobutylcarbinyl sulfonates reveal a variation of rate ratios from 6×10^5 down to as low as 12 (Table 4). The major cause for this wide span seems to be the degree of σ-participation in the reaction of the cyclobutylcarbinyl substrates, whereas in the case of the bicyclobutylcarbinyl substrates a rather stable cation always results, either of the cyclopropylcarbinyl type (**34** and the tricycloheptenyl cation derived from **4**[2]) or a nonclassical cation of the bishomocyclopropenyl type (*ax*-**31** and the cations derived from **1**, **2**,[1] and **3**[2]).

Experimental Section

General Remarks: NMR: Bruker AC 200, AC 250, Avance 400 and DMX 600. Internal standards were $CHCl_3$ (δ = 7.26) and CHD_2COCD_3 (δ = 2.04) for ^1H NMR, and $CDCl_3$ (δ = 77.0) and CD_3COCD_3 (δ = 29.8) for ^{13}C NMR spectroscopy. *J* values are given in Hz. The multiplicities of the signals are abbreviated as s (singlet), d (doublet), t (triplet), q (quadruplet), quint (quintuplet), sext (sextuplet), sept (septuplet), m (multiplet), br (broad) and combinations thereof. Multiplicities in the ^{13}C NMR spectra are only given for those cases for which proton coupling has been determined. Otherwise, the assignments are based on a DEPT sequence or a C,H COSY spectrum. − IR: Perkin−Elmer 1420 ratio recording infrared spectrophotometer and 1605 FT-IR spectrometer. − MS: Finnigan MAT 8200 (EI mode) and MAT 90 (CI mode and HRMS). GC−MS: Fisons GC 8000 and Fisons MD 800. − Elemental analyses: LECO CHNS 932. − Melting points: Kofler hot stage from C. Reichert, Optische Werke A. G., Wien, Austria.

(1α,2β,3α,4β)-Bicyclo[1.1.0]butane-2,4-dimethanol Dimesylate (*endo*,*endo*-9): Crude *endo*,*endo*-**9** (1.72 g) was obtained from the dialcohol *endo*,*endo*-**8** (1.00 g), according to the procedure described previously.[6] At variance with the earlier experiment, it turned out to be a yellowish solid. Dissolution in CH_2Cl_2/light petroleum ether (referring to the fraction with b.p. 30−50 °C, LP) and cooling to −30 °C provided pure *endo*,*endo*-**9** (1.34 g, 57%) as colourless crystals, m.p. 61−62 °C. On particularly slow crystallisation, crystals suitable for X-ray analysis were formed. − ^1H NMR (200 MHz, $CDCl_3$): The data reported previously have been refined by simulation of the $A_2MM'X_2X'_2$ spectrum; δ = 1.99 [t, $J_{1,2}$ = 3.6, 2 H,1-H, 3-H (A_2)], 3.06 [m, $J_{2,4}$ = −2.5, $J_{2,CH2}$ = 7.2, 2 H, 2-H, 4-H (MM′)], 3.06 (s, 6 H, 2 CH_3), 4.28 [m, 4 H, 2 CH_2 ($X_2X'_2$)]. − ^{13}C NMR ($CDCl_3$): δ = 12.0 (C-1), 37.8 (CH_3), 51.0 (C-2), 70.2 (CH_2). − $C_8H_{14}O_6S_2$ (270.3): calcd. C 35.54, H 5.22, S 23.72; found C 35.96, H 5.26, S 23.29.

X-ray Diffraction Analysis of *endo*,*endo*-9: $C_8H_{14}O_6S_2$, *M* = 270.31, colourless block (0.4 × 0.3 × 0.3 mm), monoclinic, space group *C*2/*c*, *a* = 2291.7(8), *b* = 562.16(5), *c* = 909.1(3) pm, β = 106.04(2)°, *V* = 1.1255(5) nm^3 (from 25 reflections, 10° < θ < 15°), *Z* = 4, $\rho_{calcd.}$ = 1.595 Mg m^{-3}, μ = 0.483 mm^{-1}, *F*(000) = 568, *T* = 173(2) K. 1617 reflections collected (3.70° ≤ θ ≤ 24.97°) of which 988 were independent (R_{int} = 0.011) and used in the structure refinement. The structure was solved by direct methods[40a] and refined by full-matrix, least-squares iteration against F^2, employing all data.[40b] All non-hydrogen atoms were refined anisotropically, all hydrogen atoms were refined isotropically, geometric restraints were used to refine the methyl and methylene hydrogen atoms, the hydrogen atoms of the bicycle were refined free. *R* values: *R*1 = 0.025 [$I > 2\sigma(I)$], *wR*2 = 0.063 (all data); *GOF* = 1.107 for 101 parameters and 4 restraints; largest difference peak and hole: 0.313 and −0.342 e nm^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-150224. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-(0)1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Solvolyses of the Dimesylate *endo*,*endo*-9: The dimesylate *endo*,*endo*-**9** and 4 equiv. of triethylamine were dissolved in 13.5 mL of the respective solvent per mmol of *endo*,*endo*-**9** and heated at 40 °C (bath temperature) for 3 d. Volatile components of the mixture were then evaporated in vacuo. The residue was treated with brine and the mixture thoroughly extracted with *tert*-butyl methyl ether (MTBE). After drying of the combined extracts with $MgSO_4$, they were concentrated in vacuo. The ratio of the products was determined by a ^1H NMR spectrum of the crude product, which was then purified by flash chromatography on SiO_2.

a) 60% Aqueous Acetone: The crude product obtained from *endo*,*endo*-**9** (1.00 g, 3.70 mmol) gave, after chromatography with MTBE as eluant, in order of elution, *cis*-5-hydroxycyclopent-2-ene-1-methanol α-mesylate (*cis*-**10a**) (417 mg, 59%) as a yellow liquid and a 3:1 mixture of *trans*-5-hydroxycyclopent-2-ene-1-methanol α-mesylate (*trans*-**10a**) and *cis*-**10a** (36 mg, 5%) as a colourless liquid. − ^1H, ^{13}C NMR: Table 1 and Table 2. − ***cis*-10a:** IR (film): $\tilde{\nu}$ = 3203−3118 cm^{-1} (br, O−H). − $C_7H_{12}O_4S$ (192.2): calcd. C 43.74, H 6.29, S 16.68; found C 43.42, H 6.56, S 16.47. − In the crude product, the ratio of *cis*-**10a**/*trans*-**10a**/*cis*-**11** was determined by NMR to be 28:1:2.

b) Ethanol: The crude product obtained from *endo*,*endo*-**9** (500 mg, 1.85 mmol) gave, after chromatography with LP/MTBE (1:1), in order of elution, pure *cis*-5-ethoxycyclopent-2-ene-1-methanol mesylate (*cis*-**10b**) (185 mg, 45%), *trans*-5-ethoxycyclopent-2-ene-1-methanol mesylate (*trans*-**10b**) (16 mg, 4%), and a 3:1 mixture of *cis*- and *trans*-5-hydroxycyclopent-2-ene-1-methanol dimesylate (*cis*- and *trans*-**11**) (33 mg, 7%) as brownish liquids. − ^1H, ^{13}C NMR: Table 1 and Table 2. − ***cis*-10b:** MS (CI, 70−100 eV, CH_4); *m*/*z* (%): 221 (48) [M + H$^+$], 125 (100), 97 (14), 81 (33), 79 (18). − $C_9H_{16}O_4S$ (220.3): calcd. C 49.07, H 7.32, S 14.56; found C 49.24, H 7.11, S 14.42. − In the crude product, the ratio of *cis*-**10b**/*trans*-**10b**/*cis*-**11**/*trans*-**11** was determined by NMR to be 25:5:3:1.

c) 2,2,2-Trifluoroethanol: The crude product obtained from *endo*,*endo*-**9** (180 mg, 0.67 mmol) gave, after chromatography with LP/MTBE (1:1), in order of elution, *cis*-5-(2,2,2-trifluoroethoxy)cyclopent-2-ene-1-methanol mesylate (*cis*-**10c**) (24 mg, 13%) and a 3:2 mixture of *cis*-**10c** and *trans*-5-(2,2,2-trifluoroethoxy)cyclopent-2-ene-1-methanol mesylate (*trans*-**10c**) (26 mg, 14%). Subsequent elution with methanol afforded 15 mg of a mixture containing *cis*-**11** as major component and unidentified compounds. − ^1H, ^{13}C NMR: Table 1 and Table 2. − ***cis*-10c:** MS (CI, 70−100 eV, CH_4); *m*/*z* (%): 275 (3) [M + H$^+$], 179 (100), 79 (60). − HRMS (CI, 70−100 eV, CH_4; [M + H$^+$], $C_9H_{14}F_3O_4S$): calcd. 275.0565, found 275.0563. − In the crude product, the ratio of *cis*-**10c**/*trans*-**10c**/*cis*-**11** was determined by NMR to be 4:1:1.

***cis*-5-Hydroxycyclopent-2-ene-1-methanol Dimesylate (*cis*-11):** A mixture of the alcohol *cis*-**10a** (140 mg, 0.73 mmol), methanesul-

fonyl chloride (92 mg, 0.80 mmol), and triethylamine (222 mg, 2.20 mmol) in 3.3 mL of CH_2Cl_2 was stirred at 0 °C under nitrogen until *cis*-**10a** had been consumed completely (5 h, monitoring by TLC on SiO_2 using ethyl acetate). After addition of some CH_2Cl_2, the mixture was extracted thoroughly with cold water (5 °C). The organic phase was dried with Na_2SO_4 and concentrated in vacuo. Purification of the residue by flash chromatography (SiO_2, MTBE) gave 152 mg (77%) of *cis*-**11** as a brownish oil. − ^{1}H, ^{13}C NMR: Table 1 and Table 2. − MS (CI, 70−100 eV, CH_4), *m/z* (%): 271 (100) [M + H$^+$], 193 (12), 175 (58), 97 (16). − $C_8H_{14}O_6S_2$ (270.3): calcd. C 35.54, H 5.22, S 23.72; found C 35.50, H 5.30, S 23.67.

Treatment of *cis*-11 with Ethanol: The dimesylate *cis*-**11** was exposed to the conditions for the ethanolysis of *endo*,*endo*-**9** (ethanol, triethylamine, 40 °C, 3 d), followed by the same workup procedure; the ^{1}H NMR spectrum of the crude product showed only the presence of *cis*-**11**; no signals due to *trans*-**10b** and *trans*-**11** were discernible.

6-Oxabicyclo[3.2.0]hept-2-ene (12): A mixture of *cis*-**10a** (100 mg, 0.52 mmol) and potassium hydride (56 mg, 1.40 mmol) in [D_8]THF (1.0 mL) was stirred at room temperature under nitrogen until *cis*-**10a** had been consumed completely (1 h, monitoring by TLC on SiO_2 using MTBE). The volatile components were then evaporated in vacuo at room temperature, condensed in a receiver cooled with liquid nitrogen and shown by NMR spectroscopy to be virtually pure **12** in [D_8]THF. The majority of the solvent was then evaporated at 30 °C/200 mbar and the residue subjected to further spectroscopic analysis. − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.56 (dm, $J_{4,4}$ = 18.2, 1 H) and 2.59 (br d, $J_{4,4}$ = 18.2, 1 H) (4-H_2), 3.58 (m, 1 H, 1-H), 4.18 (dd, $J_{7,7}$ = 5.5, $J_{1,7}$ = 3.3, 1 H) and 4.98 (t, average of $J_{7,7}$ and $J_{1,7}$ = 6.0, 1 H) (7-H_2), 5.46 (br t, average of $J_{1,5}$ and $J_{4exo,5}$ = 4.6, 1 H, 5-H), 5.92 (dq, $J_{2,3}$ = 5.7, J = 2.1, 1 H) and 6.00 (dm, $J_{2,3}$ = 5.7, 1 H) (2-H, 3-H); the assignment is based on a H,H COSY spectrum. − ^{13}C NMR (151 MHz, $CDCl_3$): δ = 41.8 (C-4), 46.1 (C-1), 78.7 (C-7), 85.7 (C-5), 131.1 and 131.9 (C-2, C-3); the assignment is based on a C,H COSY spectrum. − HRMS (EI, 70 eV; [M$^+$], C_6H_8O): calcd. 96.0575; found 96.0571.

(1α,2α,3α,4β)-[(2,4-Dibromo-1,3-cyclobutanediyl)bis(methylenoxy)]-bis(trimethylsilane) (14b): A solution of (1α,2α,3α,4β)-2,4-dibromocyclobutane-1,3-dimethanol[14] (**13**; 2.00 g, 7.30 mmol), anhydrous triethylamine (3.72 g, 36.8 mmol) and freshly distilled Me_3SiCl (2.38 g, 21.9 mmol) in anhydrous CH_2Cl_2 (400 mL) was stirred at 20 °C under nitrogen until **13** had been consumed completely (3 h, monitoring by TLC on SiO_2 with MTBE). The mixture was then extracted with water (3 × 60 mL) and brine (40 mL), dried with $MgSO_4$ and concentrated in vacuo. The residue was filtered through SiO_2 with MTBE as eluant to give **14b** as a yellow oil (2.73 g, 89%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.13 (s, 18 H, 6 CH_3), 2.87 (dddd, $J_{1,2}$ and $J_{1,4}$ = 9.4, 7.2, $J_{1,CH2}$ = 7.9, 5.3, 2 H, 1-H, 3-H), 3.72 (dd, ^2J = 10.8, ^3J = 5.3, 2 H) and 3.79 (dd, ^2J = 10.8, ^3J = 7.9, 2 H) (2 CH_2), 3.81 (t, J = 9.4, 1 H) and 4.83 (t, J = 7.2, 1 H) (2-H, 4-H). − ^{13}C NMR (51 MHz, $CDCl_3$): δ = −0.5 (CH_3), 41.8, 52.0 (C-2, C-4), 50.9 (C-1, C-3), 61.8 (CH_2). − $C_{12}H_{26}Br_2O_2Si_2$ (418.3): calcd. C 34.46, H 6.26; found C 33.98, H 6.22.

(1α,2α,3α,4α)-[(Bicyclo[1.1.0]butane-2,4-diyl)bis(methylenoxy)]-bis(trimethylsilane) (*exo*,*exo*-15b): *tert*-Butyllithium (12.0 mmol, 10.3 mL, 1.17 M in pentane) was added dropwise over 10 min to a stirred solution of **14b** (2.00 g, 4.78 mmol) in anhydrous diethyl ether (165 mL), kept under nitrogen at −78 °C. Stirring was continued for 3.5 h at −78 °C. The mixture was then treated with water (1.5 mL) and allowed to warm to 20 °C. After extraction with water (3 × 100 mL), the organic solution was dried with $MgSO_4$ and concentrated in vacuo. The remaining yellow oil (1.24 g) was shown by ^{1}H NMR spectroscopy to be a 2:1 mixture of *exo*,*exo*-**15b** (60%) and (1α,2α,3α)-[(2-bromo-1,3-cyclobutanediyl)bis(methylenoxy)]-bis(trimethylsilane) (**18**; 30%) containing some impurities. − MS (CI, 120−150 eV, CH_4): *m/z* (%): 341, 339 (17, 19) ([M + H$^+$] for **18**), 259 (78) ([M$^+$ − Br] for **18** and/or [M + H$^+$] for *exo*,*exo*-**15b**), 169 (100) ([M$^+$ − Me_3SiO] for *exo*,*exo*-**15b**). − HRMS (CI, 70 eV, CH_4; [M$^+$ − Br] for **18** and/or [M + H$^+$] for *exo*,*exo*- **15b**, $C_{12}H_{27}O_2Si_2$): calcd. 259.1550; found 259.1548. − ***exo*,*exo*-15b:** ^{1}H NMR (200 MHz, $CDCl_3$): The AA′$M_2X_2X_2'$ spectrum has been simulated; δ = 0.10 (s, 18 H, 6 CH_3), 1.17 ("t"m, $J_{2,CH2}$ = 5.5, $J_{1,2}$ = 0.9, $J_{2,4}$ = 0.6, 2 H, 2-H, 4-H), 1.43 (t, $J_{1,2}$ = 0.9, 2 H, 1-H, 3-H), 3.49 ("d", ^3J = 5.5, 4 H, 2 CH_2). − ^{13}C NMR (101 MHz, $CDCl_3$): δ = −0.45 (CH_3), 3.8 (C-1), 42.9 (C-2), 62.0 (CH_2). − **18:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.12 (s, 18 H, 6 CH_3), 1.69 (q, average of $J_{1,4}$, $J_{3,4}$ and $J_{4,4}$ = 9.9, 1 H) and 2.04 (q, average of $J_{1,4}$, $J_{3,4}$ and $J_{4,4}$ = 9.5, 1 H) (4-H_2), 2.57 (qt, average of 2 $J_{1,4}$ and $J_{1,2}$ = 9.2, average of 2 $J_{1,CH2}$ = 4.3, 2 H, 1-H, 3-H), 3.53 (dd, ^2J = 11.1, ^3J = 4.0, 2 H) and 3.59 (dd, ^2J = 11.1, ^3J = 4.6, 2 H) (2 CH_2), 4.10 (t, $J_{1,2}$ = 8.5, 1 H, 2-H). − ^{13}C NMR (101 MHz, $CDCl_3$): δ = −0.51 (CH_3), 23.1 (C-4), 42.7 (C-2), 46.4 (C-1, C-3), 61.8 (CH_2). − As the next experiment proves, the product mixture must have contained some *endo*,*endo*-**15b**, but its NMR signals could not be discerned with certainty. In a series of experiments, the majority proceeded as described above, but in several cases [(*cis*-1,3-cyclobutanediyl)bis(methylenoxy)]bis(trimethylsilane) (**19**) must have been produced instead of **18**. This was evident from the preparation of the dimesylate *exo*,*exo*-**9** (see below), which was accompanied by the dimesylate **23**.

(1α,2α,3α,4α)-Bicyclo[1.1.0]butane-2,4-dimethanol (*exo*,*exo*-8): A 2:1 mixture of *exo*,*exo*-**15b** (749 mg, 2.90 mmol) and **18** (491 mg, 1.45 mmol), as obtained from the preceding experiment, was dissolved in methanol. After addition of K_2CO_3 (46 mg, 0.33 mmol), the mixture was stirred at 20 °C for 3 h and then concentrated in vacuo. The treatment of the residue with acetone resulted in a suspension, which was filtered. Concentration of the filtrate in vacuo gave a yellow oil (584 mg), which was analysed by NMR spectroscopy. It contained *exo*,*exo*-**8** (58%) and *endo*,*endo*-**8** (7%), together with (1α,2α,3α)-2-bromocyclobutane-1,3-dimethanol (**20**; 29%) in a ratio of 8:1:4 as major components, and also some impurities. − MS (CI, 120−150 eV, CH_4): *m/z* (%): 197, 195 (8, 8) ([M + H$^+$] for **20**), 161 (11), 159 (11), 135 (12), 117 (16), 115 (11) ([M$^+$ − Br] for **20** and/or [M + H$^+$] for *exo*,*exo*-**8**), 97 (100) ([M$^+$ − OH] for *exo*,*exo*-**8**), 81 (43), 79 (72), 69 (32), 67 (33), 57 (18), 55 (8). − MS (EI, 70 eV); *m/z* (%): 114 (1) ([M$^+$] for *exo*,*exo*-**8**), 95 (12), 83 (25), 81 (10), 79 (23), 70 (12), 69 (15), 68 (22), 67 (100), 66 (19), 65 (19), 59 (17), 57 (50), 55 (46), 53 (25), 44 (12), 43 (42), 42 (16), 41 (87), 40 (14), 39 (65). − IR (film): $\tilde{\nu}$ = 3328 cm^{-1} (br, O−H). − ***exo*,*exo*-8:** ^{1}H NMR [400 (600) MHz, $CDCl_3$ (CD_3COCD_3)]: The coupling constants are based on the simulation of the spectrum of *exo*,*exo*-**15b**; δ = 1.17 (1.08) ("t"m, $J_{2,CH2}$ = 5.5, $J_{1,2}$ = 0.8, $J_{2,4}$ = 0.6, 2 H, 2-H, 4-H), 1.49 (1.46) (t, $J_{1,2}$ = 0.8, 2 H, 1-H, 3-H), 3.48 (3.42) ("d", $J_{2,CH2}$ = 5.5, 4 H, 2 CH_2). − ^{13}C NMR [101 (151) MHz, $CDCl_3$ (CD_3COCD_3)]: δ = 3.2 (3.7), (dsext, $^1J_{C,H}$ = 203, $J_{C,H}$ = 4, C-1), 42.8 (44.2) (dsext, $^1J_{C,H}$ = 166, $^2J_{C,H}$ = $^3J_{C,H}$ = 3, C-2), 61.7 (61.7) (t, $^1J_{C,H}$ = 139, CH_2). − **20:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.71 (q, average of $J_{1,4}$, $J_{3,4}$ and $J_{4,4}$ = 10.1, 1 H) and 2.08 (q, average of $J_{1,4}$, $J_{3,4}$ and $J_{4,4}$ = 9.6, 1 H) (4-H_2), 2.61 (qt, average of 2 $J_{1,4}$ and $J_{1,2}$ = 9.1, 2 $J_{1,CH2}$ = 4.3, 2 H, 1-H, 3-H), 3.54 (dd, ^2J = 11.6, ^3J = 4.3, 2 H) and 3.61 (dd, ^2J = 11.6, ^3J = 4.3, 2 H) (2 CH_2), 4.18 (t, $J_{1,2}$ = 8.6, 1 H, 2-H). − ^{13}C NMR (101 MHz, $CDCl_3$): δ = 22.5 (C-4), 42.8 (C-2), 46.2 (C-1,

C-3), 61.7 (CH_2). − The product ratio given above was subject to substantial variation in different experiments. When the starting material contained **19** instead of **18** (see comment at the end of the preceding experiment), the mixture of dialcohols consisted of *exo*,*exo*-**8**, *endo*,*endo*-**8** and **22**.

(1α,2α,3α,4α)-Bicyclo[1.1.0]butane-2,4-dimethanol Dimesylate (*exo*,*exo*-9): A mixture of the dialcohols *exo*,*exo*-**8** (major component), **22** and *endo*,*endo*-**8** (minor component) (990 mg, ca. 8.6 mmol), as obtained from an experiment of the preceding type, was dissolved in anhydrous CH_2Cl_2 (50 mL) under nitrogen. Anhydrous triethylamine (2.53 g, 25.0 mmol) was added, followed dropwise with stirring, at −30 °C over 10 min, by freshly distilled methanesulfonyl chloride (2.54 g, 22.2 mmol). Stirring was continued for 5 h, during which period the mixture was allowed to warm to 0 °C. After extraction with ice-cold water (4 × 40 mL), the solution was dried with $MgSO_4$ and concentrated in vacuo at 5 °C. The remaining oil was dissolved in the minimum quantity of CH_2Cl_2/LP (1:1). On storage of this solution at −30 °C over 3 d, yellow crystals precipitated (1.40 g, ca. 60%); these were shown by NMR spectroscopy to consist virtually entirely of a mixture of *exo*,*exo*-**9**, *endo*,*endo*-**9** and *cis*-cyclobutane-1,3-dimethanol dimesylate (**23**) in a ratio of 36:1:16. − Mixture of $C_8H_{14}O_6S_2$ (270.3, 37 parts) and $C_8H_{16}O_6S_2$ (272.3, 16 parts): calcd. C 35.46, H 5.43, S 23.66; found C 35.62, H 5.45, S 23.24. − ***exo*,*exo*-9:** ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.33 (br "t", $J_{2,CH2}$ = 6.0, 2 H, 2-H, 4-H), 1.98 (br s, 2 H, 1-H, 3-H), 3.01 (s, 6 H, 2 CH_3), 4.10 ("d", $J_{2,CH2}$ = 6.0, 4 H, 2 CH_2). − ^{13}C NMR (151 MHz, $CDCl_3$): δ = 5.2 (dsext, $^1J_{C,H}$ = 210, $J_{C,H}$ = 4, C-1), 37.7 (ddquint, $^1J_{C,H}$ = 173, $^3J_{C,H}$ = 5, $^2J_{C,H}$ = 3, C-2), 37.8 (q, $^1J_{C,H}$ = 139, CH_3), 68.3 (br t, $^1J_{C,H}$ = 150, CH_2). − **23:** ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.73 (tm, ^3J = 9.0, 2 H, 2-H, 4-H), 2.23 (tm, ^3J = 9.0, 2 H, 2-H, 4-H), 2.65 (quint of t, 4 $J_{1,2}$ = 9.0, 2 $J_{1,CH2}$ = 5.9, 2 H, 1-H, 3-H), 3.00 (s, 6 H, 2 CH_3), 4.13 (d, $J_{1,CH2}$ = 5.9, 4 H, 2 CH_2). − ^{13}C NMR (151 MHz, $CDCl_3$): δ = 26.6 (C-2), 29.9 (C-1), 37.3 (CH_3), 72.6 (CH_2).

Solvolyses of the Dimesylate *exo*,*exo*-9: The 36:1:16 mixture of the dimesylates *exo*,*exo*-**9**, *endo*,*endo*-**9** and **23** was subjected to solvolysis conditions as in the case of pure *endo*,*endo*-**9**. Attempts to purify a consecutive product of *exo*,*exo*-**9** were unsuccessful; only the crude products could therefore be analysed.

a) Ethanol: After 3 and 7 d, respectively, at 40 °C, *exo*,*exo*-**9** was consumed to the extents of approximately 30 and 50%, determined by using the intensity of the signals of **23** as internal standard. The yields of (1α,2α,3α,4α)-4-(ethoxymethyl)bicyclo[1.1.0]butane-2-methanol mesylate (**26**) amounted to approximately 70 and 50%, respectively, of the starting material consumed. − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.19 (t, J = 7.0, 3 H, CH_2CH_3) 1.20−1.31 (in this region, the signals of 2-H and 4-H are superimposed on by signals of impurities), 1.75 (br s, 2 H, 1-H, 3-H), 3.01 (s, 3 H, SCH_3), 3.34 (d, $J_{4,CH2}$ = 5.8, 2 H, $CHCH_2OCH_2$), 3.46 (q, J = 7.0, 2 H, CH_2CH_3), 4.09 (d, $J_{2,CH2}$ = 6.3, 2 H, CH_2OS). − ^{13}C NMR (151 MHz, $CDCl_3$): δ = 4.7 (dm, $^1J_{C,H}$ = 207, C-1, C-3), 15.1 (qt, $^1J_{C,H}$ = 126, $^2J_{C,H}$ = 3, CH_2CH_3), 37.9 (q, $^1J_{C,H}$ = 139, SCH_3), 38.0 (dm, $^1J_{C,H}$ = 173, C-2), 40.2 (dm, $^1J_{C,H}$ = 169, C-4), 66.2 (tm, $^1J_{C,H}$ = 140, CH_2CH_3), 69.1 (tm, $^1J_{C,H}$ = 150, CH_2OS), 69.3 (tm, $^1J_{C,H}$ = 139, $CHCH_2OCH_2$).

b) 2,2,2-Trifluoroethanol: After 3 d at 40 °C, *exo*,*exo*-**9** was consumed to the extent of approximately 20%. The yield of (1α,2α,3α,4α)-4-(2,2,2-trifluoroethoxymethyl)bicyclo[1.1.0]butane-2-methanol mesylate (**27**) was estimated to be ≥ 70% of the starting material consumed. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.79 (br s, 2 H, 1-H, 3-H), 3.51 (d, $J_{4,CH2}$ = 5.9, 2 H, $CHCH_2OCH_2$), 3.78 (q, $J_{H,F}$ = 8.7, 2 H, CH_2CF_3), the missing signals were superimposed by signals of *exo*,*exo*-**9**, **23** and impurities. − ^{13}C NMR (51 MHz, $CDCl_3$): δ = 4.5, 37.9, 39.1, 68.8, the missing signals were either superimposed by signals of *exo*,*exo*-**9** and **23** or not observed due to low intensity, because of the splitting due to C,F couplings.

(1α,2α,3α,4α)-2,4-Bis(ethoxymethyl)bicyclo[1.1.0]butane (25): A 2:1 mixture (200 mg) of *exo*,*exo*-**8** (0.94 mmol) and **20** (0.47 mmol), dissolved in anhydrous THF (8 mL), was added dropwise to a stirred suspension of NaH (168 mg, 7.00 mmol) in anhydrous THF (3 mL), at 20 °C under nitrogen. Iodoethane (1.09 g, 7.00 mmol) was added dropwise to the resulting mixture, with continued stirring. The mixture was then refluxed for 16 h and thereafter treated cautiously with water (20 mL). After extraction with ether (3 × 20 mL), the combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. The remaining yellow oil (156 mg) was shown by NMR spectroscopy to consist of **25** (56%) and (1α,2α,3α)-2-bromo-1,3-bis(ethoxymethyl)cyclobutane (**21**; 56%) in a ratio of 2:1 as major components, together with some impurities. − MS (CI, 120−150 eV, isobutane); *m*/*z* (%): 253 (65), 251 (68) ([M + H$^+$] for **21**), 229 (17), 217 (14), 215 (17), 199 (14), 171 (100) ([M$^+$ − Br] for **21** and/or [M + H$^+$] for **25**), 169 (17), 137 (18), 127 (23), 125 (39), 81 (20). − MS (EI, 70 eV); *m*/*z* (%): 170 (3) ([M$^+$] for **25**), 111 (38), 98 (21), 96 (27), 85 (27), 83 (100), 81 (34), 79 (37), 70 (25), 67 (49), 59 (56), 57 (43), 55 (44), 43 (32), 41 (61), 39 (27). − **25:** ^{1}H NMR (600 MHz, $CDCl_3$): 1.19 (t, J = 7.0, 6 H, 2 CH_3), 1.19 (m, 2 H, 2-H, 4-H, proven by a C,H COSY spectrum), 1.50 (t, $J_{1,2}$ = 0.8, 2 H, 1-H, 3-H), 3.33 ("d", $J_{2,CH2}$ = 5.8, 4 H, 2 $CHCH_2$), 3.45 (q, J = 7.0, 4 H, CH_3CH_2). − ^{13}C NMR (151 MHz, $CDCl_3$): δ = 4.0 (dm, $^1J_{C,H}$ = 204, C-1), 15.1 (qt, $^1J_{C,H}$ = 126, $^2J_{C,H}$ = 4, CH_3), 40.4 (dm, $^1J_{C,H}$ = 168, C-2), 65.9 (tq, $^1J_{C,H}$ = 140, $^2J_{C,H}$ = 4, CH_2CH_3), 69.8 (tm, $^1J_{C,H}$ = 140, $CHCH_2$). − HRMS (EI, 70 eV; [M$^+$], $C_{10}H_{18}O_2$) calcd. 170.1307; found 170.1304. − **21:** ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (t, J = 7.0, 6 H, 2 CH_3), 1.61 (q, average of $J_{1,4}$, $J_{3,4}$ and $J_{4,4}$ = 9.8, 1 H) and 2.17 (q, average of $J_{1,4}$, $J_{3,4}$ and $J_{4,4}$ = 9.4, 1 H) (4-H_2), 2.65 (qt, average of 2 $J_{1,4}$ and $J_{1,2}$ = 9.1, average of 2 $J_{1,CH2}$ = 8.5, 2 H, 1-H, 3-H), 3.39−3.60 (m, 8 H, 2 $CHCH_2O$, 2 CH_3CH_2), 4.06 (t, $J_{1,2}$ = 8.5, 1 H, 2-H). − ^{13}C NMR (101 MHz, $CDCl_3$): δ = 15.0 (CH_3), 25.2 (C-4), 44.2 (C-2), 44.8 (C-1, C-3), 66.4 (CH_3CH_2), 70.5 ($CHCH_2$).

Treatment of 25 with a Triethylamine/Triethylammonium Mesylate Buffer: A 2:1 mixture (100 mg) of **25** (0.34 mmol) and **21** (0.17 mmol), together with anhydrous triethylamine (119 mg, 1.18 mmol), was dissolved in anhydrous ethanol (7 mL). At 20 °C, a mixture of anhydrous triethylamine (119 mg, 1.18 mmol) and methanesulfonic acid (113 mg, 1.18 mmol) was added dropwise to this stirred solution over several minutes. After 1 h at 20 °C, half of the mixture was concentrated in vacuo. Brine (10 mL) was added to the stirred residue and the mixture was then extracted with MTBE (4 × 10 mL). The combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. According to NMR spectroscopic analysis, the remaining yellow oil (51 mg) no longer contained any **25**. The signals observed in addition to those of **21** indicated that ethanol had added to **25**, with formation of a mixture of two cyclopropylcarbinyl derivatives.

Ethanolysis of *cis*-Cyclobutane-1,3-dimethanol Ditosylate (28): A stirred solution of **28**[19−21] (1.60 g, 3.77 mmol) in anhydrous ethanol (80 mL) was heated at 80 °C (bath temperature) under nitrogen for 7 d. The mixture was then concentrated in vacuo and the residue was extracted with diethyl ether (50 mL). The ether solution was washed with saturated aqueous $NaHCO_3$ (2 × 30 mL) and

then with brine (30 mL). After drying with $MgSO_4$, the solution was concentrated in vacuo and the residue was subjected to distillation to give a colourless liquid (120 mg, 18%), b.p. 75 °C (kugelrohr)/15 mbar, which was shown by NMR spectroscopy to contain essentially two compounds: namely **24** and 1-ethoxy-3-(ethoxymethyl)cyclopentane (*major*-**29**) in a ratio of ca. 10:7. Analysis by GC-MS coupling [capillary column (30 m) coated with Carbowax; temperature of the column: 50 °C (3 min), then increase of the temperature by 4 °C per min up to 240 °C] revealed the presence of **24** (retention time 14.1 min), *minor*-**29** (14.5 min) and *major*-**29** (14.6) in the ratio of 10:1:7 and ca. 10% impurities. − **24:** See next experiment. − ***major*-29:** ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.17, 1.19 (2 × t, J = 7.0, 2 × 3 H, 2 CH_3), 1.25 (m, 1 H, 4-H), 1.44 (m, 1 H, 2-H), 1.64 (m, 1 H, 5-H), 1.80−1.91 (m, 3 H, 2-H, 4-H, 5-H), 2.37 (sept, average of $J_{2,3}$, $J_{3,4}$ and $J_{3,CH2}$ = 7.5, 1 H, 3-H), 3.28 (d, $J_{3,CH2}$ = 6.9, 2 H, CHCH_2O), 3.40−3.49 (m, 4 H, 2 CH_2CH$_3$), 3.91 (m, 1 H, 1-H); the assignment is based on H,H and C,H COSY spectra. − ^{13}C NMR (101 MHz, $CDCl_3$): δ = 15.2 (CH_3), 15.5 (CH_3), 27.2 (C-4), 32.0 (C-5), 35.9 (C-2), 37.3 (C-3), 63.9 (CHO*C*H$_2$), 66.2 (CH$_2$O*C*H$_2$CH$_3$), 75.0 (CH*C*H$_2$O), 80.6 (C-1). − MS (EI, 70 eV); *m*/*z* (%): 143 (12), 126 (11), 113 (22), 98 (22), 97 (20), 85 (100), 83 (16), 82 (23), 81 (28), 79 (14), 70 (11), 69 (16), 67 (38), 59 (24), 57 (52), 55 (17), 44 (10), 43 (18), 41 (31). − ***minor*-29:** MS (EI, 70 eV); *m*/*z* (%): 143 (10), 113 (11), 98 (11), 97 (12), 85 (100), 82 (14), 81 (18), 79 (10), 69 (26), 59 (17), 57 (41), 55 (11), 43 (15), 41 (21).

***cis*-1,3-Bis(ethoxymethyl)cyclobutane (24):** A solution of **22**[6,19−21] (600 mg, 5.16 mmol) and iodoethane (3.18 g, 20.4 mmol) in anhydrous THF (10 mL) was added dropwise to a suspension of NaH (490 mg, 20.4 mmol) in anhydrous THF (20 mL), stirred at 40 °C under nitrogen. The resulting mixture was then heated at reflux for 8 h and thereafter treated cautiously with water (40 mL). The resulting layers were separated and the aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with water (3 × 20 mL), dried with $MgSO_4$ and concentrated at 0 °C/15 mbar. By distillation from the residue, **24** (420 mg, 47%) was obtained as an orange oil, b.p. 100 °C (kugelrohr)/15 mbar. − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.17 (t, 6 H), 3.45 (q, 4 H) (J = 7.0, 2 CH_3CH_2), 1.45 (tm, $J_{1,2}$ = 8.9, 2 H), 2.16 (tm, $J_{1,2}$ = 8.1, 2 H) (2-H$_2$, 4-H$_2$), 2.45 (ttt, $J_{1,2}$ = 8.9 and 8.1, $J_{1,CH2}$ = 6.6, 2 H, 1-H, 3-H), 3.34 (d, $J_{1,CH2}$ = 6.6, 4 H, 2 CHCH_2O). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.2 (CH_3), 28.9 (C-2), 31.4 (C-1), 66.2 (CH_3CH_2O), 75.8 (CH*C*H$_2$O). − MS (EI, 70 eV); *m*/*z* (%): 172 (0.2)[M^+], 171 (0.5), 143 (7), 98 (10), 97 (12), 86 (9), 85 (100), 83 (9), 82 (10), 81 (15), 80 (9), 79 (18), 67 (34), 59 (33), 58 (32), 57 (76), 55 (12), 45 (9), 43 (20), 42 (8), 41 (52), 39 (17). − MS (CI, 150 eV, isobutane); *m*/*z* (%): 173 (100) [M + H^+], 145 (4), 116 (15), 114 (9), 113 (18). − HRMS (EI, 70 eV; [M^+ − H], $C_{10}H_{19}O_2$): calcd. 171.1385; found 171.1384.

Kinetic Measurements: Rate constants were determined conductimetrically, using 8-mL conductivity cells with bright platinum electrodes. Reactions were initiated by injecting 10−20 μL of a freshly prepared 1% acetonitrile solution of one of the sulfonates into the thermostatted solvolysis medium. Changes in conductance were recorded using a conductivity amplifier,[41] connected to a Solartron 7151 computing multimeter, which collected and stored voltage readings (proportional to the conductance) at predetermined time intervals. Typically, about 15 readings, equally spaced in extent of reaction, were input into the LSKIN computer program (Fortran) for first-order kinetics,[42] adapted to run on a 486 personal computer.

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