# Solvolysis of Tricyclo[3.1.0.0$^{2,6}$]hex-3-yl and Bicyclo[2.1.1]hex-2-yl Sulfonates[+]☆

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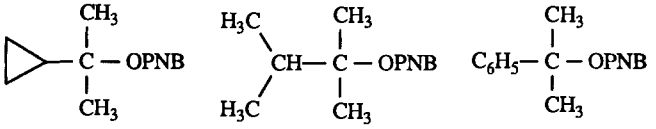
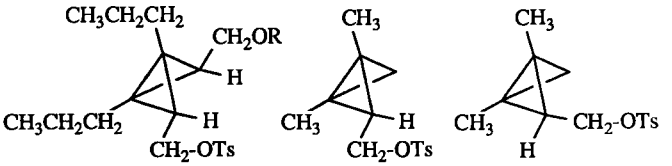
Solvolyses of *cis*-tricyclo[3.1.0.0$^{2,6}$]hex-3,4-diyl ditosylate (**12**) and *cis*-bicyclo[2.1.1]hex-2,3-diyl ditosylate (**27**) have been carried out in 80% aqueous ethanol in the presence of ethyldiisopropylamine. In the former case, *endo,endo*-tricyclo[2.2.0.0$^{2,6}$]hexane-3,5-diol (**13a**), its monoether **13b** and diether **13c** were products whereas in the latter the monoethers **28b, d, e, g** and the diethers **28a, c, f** of bicyclo[3.1.0]hexane were formed. In pure ethanol, **12** was converted into pure **13c** in good yield. In the presence of the weaker base 2,6-lutidine, the solvolysis of **12** in aqueous ethanol gave different products, i.e. *exo,exo*-4,6-diethoxybicyclo[3.1.0]hex-2-ene (**14a**) and several aldehydes, inter alia cyclopentadiene-1-carboxaldehyde (**15**). In control experiments, the tricyclic compounds **13b, c** were converted into **14a**, **15** and further aldehydes as well as into the bicyclo[2.1.1]hexene derivatives **19a, b**. Sulfonates of tricyclo[3.1.0.0$^{2,6}$]hexan-3-ol (**21a**) could not be isolated but its mesylate **21c** was characterized by NMR spectroscopy and hydrolysed in aqueous acetone to give tricyclo[2.2.0.0$^{2,6}$]hexan-*endo*-3-ol (**22a**). It is concluded from these results that the dissociations of the above sulfonates do not lead to unrearranged carbocations. Rather, they proceed with participation of the β-carbon in *trans* position relative to the leaving group resulting in the immediate generation of rearranged cations. – Kinetic studies show that the tricyclic mesylate **21c** solvolyses in 80% ethanol/water 1.4 · 10$^5$ times as fast as bicyclo[2.1.1]hex-2-yl tosylate (**25**), and the tricyclic ditosylate **12** solvolyses 6 · 10$^5$ as fast as the corresponding bicyclic ditosylate **27**. These rate enhancements are similar to those previously observed for less strained cyclopropylcarbinyl substrates.

As numerous investigations prove, esters of cyclopropylcarbinols solvolyse much faster than related alkyl esters and cycloalkylcarbinyl esters with larger rings[1]. Thus, the acceleration observed for the hydrolysis in 80% aqueous acetone of the cyclopropyldimethyl *p*-nitrobenzoate (PNB) **1** in comparison to the isopropyldimethyl derivative **2** amounts to a factor of 1.7 · 10$^5$ and even exceeds the effect of the phenyl group in **3** ($k_3/k_2 = 330$)[2].



**1** **2** **3**

Much less is known about the effect of the bicyclo[1.1.0]butane moiety in bicyclobutylcarbinyl esters. Breslow et al.[3] have studied the tosylates **4–6**. Although the solvolysis products no longer contained a three-membered ring, none of these compounds reacted more rapidly than simple cyclopropylcarbinyl tosylates[1b].



R = H: **4a** **5** **6**
R = Ts: **4b**

The first substrates with bridged bicyclobutane subunits were solvolysed by Masamune et al.[4] The comparison of the rate constants of **7** and **8** reveals an enormous acceleration as consequence of the shortening of the bridge across the bicyclobutane system. A rate factor of 2 · 10$^4$ was estimated[4], but 10$^5$ seems to be more appropriate on the basis of a recently determined *p*-toluenesulfonate/*p*-nitrobenzoate rate ratio[5].

The high reactivity of the tricyclopentyl skeleton was corroborated by studies of the benzoate **9**[6] which readily undergoes isomerisation to **10**. The cation generated either from **9** or **10** is a dimethyl derivative of the $(CH)_5$ cation, for which quantumchemical calculations predicted the structure of a square pyramid[7]. NMR spectra of substituted derivatives of this cation reveal dynamic phenomena indi-

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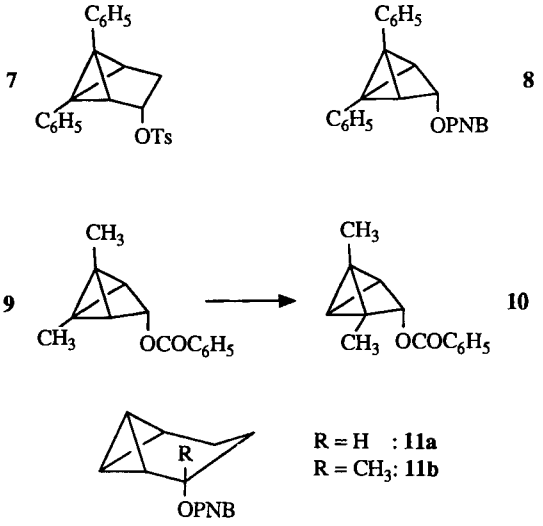
cating that equilibrations do not interchange the positions of all equally substituted carbon atoms[8].




Yano and Yoshida[9] hydrolysed the tricycloheptyl *p*-nitrobenzoates **11**. In 60% aqueous acetone, the rate constants were determined to be $2.26 \cdot 10^{-5}$ (**11a**, 80°C) and $6.90 \cdot 10^{-4}$ $s^{-1}$ (**11b**, 50°C). From these values, a $CH_3$/H ratio of only 3200 was calculated. In comparison to model systems with $CH_3$/H ratios of up to $10^8$, this factor supports a strong anchimeric participation of the bicyclobutane subunit in the dissociation of the substrates **11**. The products formed are *anti*-7-norbornenol and *exo*-2-methylbicyclo[3.2.0]hept-6-en-2-ol. Thus, the 7-norbornenyl cation and its 1-methyl derivative, respectively, should be the intermediates. The reaction rates of **11a** and **11b** resemble those of cyclopropylmethylcarbinyl *p*-nitrobenzoate and **1**, respectively, rather closely.

We now report product studies and rate constants for solvolyses of the mesylate **21c** of tricyclohexanol **21a** and the corresponding *cis*-ditosylate **12**. By way of comparison, we use the results of analogous experiments with bicyclo[2.1.1]hex-2-yl tosylate (**25**) and -2,3-diyl ditosylate (**27**).

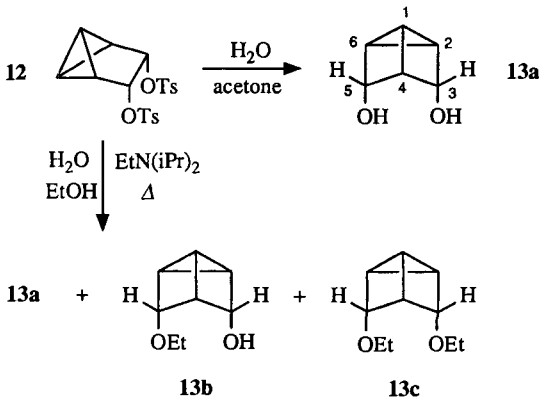
## Results and Discussion

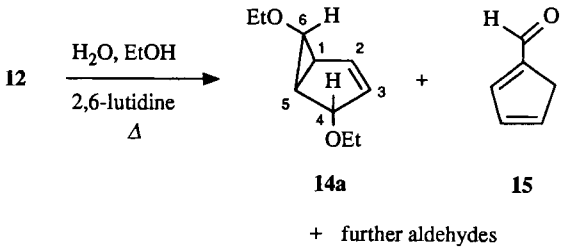
### 1. Product Studies

The solvolysis of ditosylate **12** in 80% aqueous ethanol in the presence of ethyldiisopropylamine at 75°C afforded a high yield of a 1.0:3.9:3.3 mixture of **13a**, its monoethyl (**13b**) and its diethyl ether (**13c**), analogous to the hydrolysis in 60% aqueous acetone leading to a 38% yield of the rearranged tricyclohexanediol **13a**[10]. In pure ethanol as solvent, pure **13c** was obtained in 83% yield.

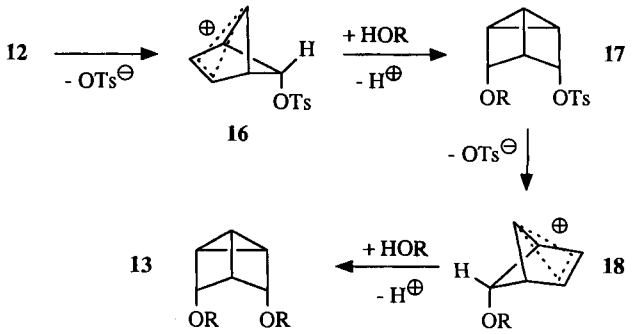
In the presence of the weaker base 2,6-lutidine, other compounds were formed. We isolated the diethoxybicyclohexene **14a** in 15% yield. In addition to the signals of **14a**, the $^1$H-NMR spectrum of the crude product showed the absorptions of six aldehydes (ratio **14a**:aldehydes = 1.0:1.6) at $\delta = 9.61 - 9.99$, which have not been identified except the known 1,3-cyclopentadiene-1-carboxaldehyde[11] (**15**).

NMR data supporting the configuration of **13a** have been discussed previously[10,12]. On the basis of the criteria derived there, no doubts remain as to the structure of **13b**, **c**. Also, the NMR data support the bicyclic carbon skeleton of **14a**. The *endo* positions of 4-H and 6-H were established by the magnitude of coupling constants of these protons and have been corroborated by NOE measurements. Saturation of 4-H gave, inter alia, an intensity enhancement of the 6-H signal of 7% and vice versa.



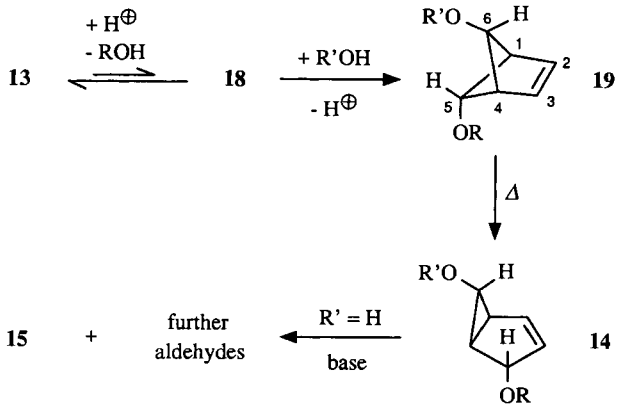




The different results of the solvolyses in the presence of bases of different strength are rationalized as follows. In both cases, the substitution of the tosylate groups should proceed according to the same mechanism, namely dissociation of **12** with participation of the bicyclobutane subunit, i.e. [1,2] migration of the bicyclobutane bridgehead-CH group being arranged *trans* relative to the leaving tosylate, to give a tosylate ion and bicyclo[2.1.1]hexen-5-yl cation **16**, trapping of **16** by ethanol or water with formation of monotosylate **17**, dissociation of **17** leading to another bicyclo-[2.1.1]hexen-5-yl cation (**18**) and a tosylate ion, and, finally, interception of **18** by the nucleophiles affording the observed products **13**.

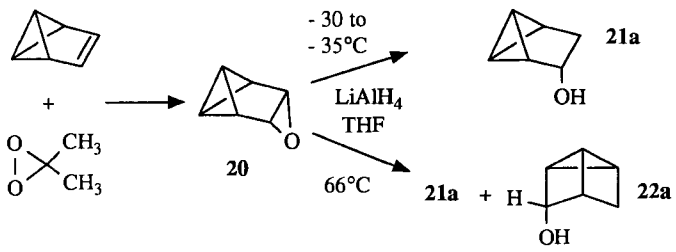


If the solvolysis mixture contains ethyldiisopropylamine the products **13** are obviously stable. This appears to be not true in the presence of 2,6-lutidine. In this case the pH of the buffer formed is lower, which may allow the establishment of the equilibrium between **13** and **18**. Under these conditions, the slower attack of the nucleophiles at the one-carbon bridge of **18** should eventually lead to the thermodynamically more stable bicyclo[2.1.1]hexenes **19**.

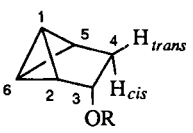
The thermal rearrangement of bicyclo[2.1.1]hexenes to bicyclo[3.1.0]hexenes is known as well as its stereochemical course[13]. Thus, the compounds **19** should be converted into the diether **14a** and the corresponding dialcohol and monoethers. Isomerization of the monoacetate of **13a** to its derivative **14** via the corresponding **19** has previously been reported[10]. Compounds **14** with a cyclopropanol subunit should be labile towards bases and, therefore, are most probably the source of the aldehydes, inter alia **15**, which is known to be unstable[11a]. The conversion of cyclopropanols into ketones and aldehydes are well-known reactions[14].



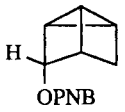

In a control experiment, we treated a mixture of the tricyclohexanes **13b, c** with hydrochloric acid and observed the bicyclo[2.1.1]hexenes **19a** (= **19**, R = R′ = OEt) and **19b** (= **19**, R = OH, R′ = OEt), the aldehyde **15**, and the diether **14a** as major products. The bicyclo[2.1.1]hexenes were identified by their characteristic NMR spectra. This finding supports our hypothesis that the tricyclohexanes **13** may be converted into the bicyclo[3.1.0]hex-2-enes **14** via the bicyclo[2.1.1]hexenes **19** on heating in a solution acidified by the 2,6-lutidine/2,6-lutidinium tosylate buffer. More direct support was obtained by heating of pure diether **13c** in 80% aqueous ethanol in the presence of the 2,6-lutidine/2,6-lutidinium tosylate buffer. The result was the same as that of the solvolysis of ditosylate **12** in 80% aqueous ethanol in the presence of lutidine, i.e. diether **14a** and several aldehydes.



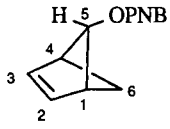

Tricyclo[3.1.0.0$^{2,6}$]hexan-3-ol (**21a**) is prepared by reduction of benzvalene oxide (**20**) with $LiAlH_4$[10]. For the preparation of **20**, *N*-benzoylpercarbamidic acid has been used[10]. We have now found that dimethyldioxirane[15] is also useful for the conversion of benzvalene into **20**. Under most conditions, reactions of **20** with $LiAlH_4$ give rise to mixtures of the tricyclohexanols **21a** and **22a**[10]. In THF as solvent at −30 to −35°C almost pure **21a** was obtained in 51% yield.




R = PNB: **21b**
R = Ms: **21c**
R = Ts: **21d**



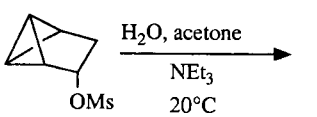

**22b**



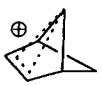

**23**

All attempts to prepare the tosylate of alcohol **21a** failed. Treatment of a mixture of **21a** and **22a** with sodium hydride and *p*-nitrobenzoyl chloride gave a small yield of the three *p*-nitrobenzoates **21b**, **22b**, and **23**. From pure **21a** under routine conditions **21b** was obtained in 22% yield.

Heating of **21b** in the presence of ethyldiisopropylamine in aqueous acetone as well as in aqueous ethanol generated very complex mixtures, the NMR spectra of which contained a signal of a *cis*-disubstituted cyclopropane subunit of the type present in **28**. This is evidence against the dissociation of **21b** to a cation and a *p*-nitrobenzoate ion as the primary process. Rather, an addition of ROH to the bicyclobutane system of **21b** is considered to be the first step.




**21c** **22a**




**24**

The reaction of **21a** with methanesulfonyl chloride (MsCl) at 0°C under routine conditions gave the mesylate **21c**, which was characterized by NMR spectroscopy at ambient temperature. Hydrolysis in 60% aqueous acetone in the presence of triethylamine at 20°C transformed **21c** rapidly to the alcohol **22a** as the sole product. This result shows that the dissociation of **21c** proceeds *with concomitant [1,2] migration of the bicyclobutane bridgehead CH group being arranged trans relative to the leaving group* and immediate formation of the bicyclo[2.1.1]hex-2-en-5-yl cation (**24**). As we have suggested in the case of the cations **16** and **18**, the attack of the nucleophile occurs at the two-carbon bridge of **24** exclusively. This appears to be the favoured site of reaction of **24** and its derivatives under kinetic control[10,13b].

Except the central bicyclobutane bond, bicyclo[2.1.1]hexane has the same carbon skeleton as tricyclo-

[3.1.0.0$^{2,6}$]hexane. Thus, we consider the bicyclo[2.1.1]hexyl tosylates **25** and **27** as the best substrates to be compared with **21c** and **12**, respectively.

Solvolyses of isotopically labeled sulfonates of bicyclo-[2.1.1]hexan-2-ol[16] and dediazoniation of isotopically labeled bicyclo[2.1.1]hex-2-yldiazonium ions revealed that the dissociation of **25** generates the nonclassical cation **26b** either directly by participation of the *trans*-methylene bridge or via the classical cation **26a**, which subsequently would have to convert rapidly into **26b**. Either of these cations is intercepted by a nucleophile with formation of a 2-substituted bicyclo[2.1.1]hexane. However, inverting substitution at C-2 plays a substantial role in the case of sulfonates as has been shown by using the optically active brosylate[16b].

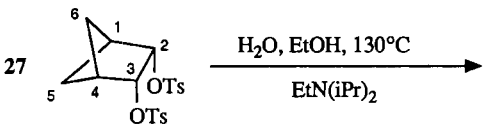

**25**

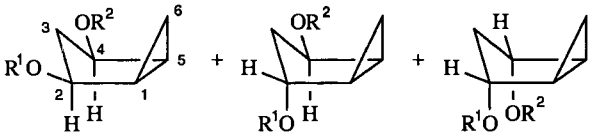
**26a**

**26b**

We have now prepared the ditosylate **27** under routine conditions by tosylation of *cis*-bicyclo[2.1.1]hexane-2,3-diol. The latter can either be obtained from bicyclo[2.1.1]hexene[17] or, more economically, from benzvalene via its *cis*-glycol[18].

The solvolysis of **27** in 80% aqueous ethanol in the presence of ethyldiisopropylamine afforded a 71% yield of all possible mono- and diethylethers (**28**) of the bicyclo-[3.1.0]hexane-2,4-diols. The diols may have been lost in the aqueous workup. There is evidence for one of them in the $^{13}$C-NMR spectrum of the crude product. By flash chromatography and gas chromatography the almost pure components **28a**, **b**, **c**, **g** and mixtures of **28d**, **e** and **28a**, **c**, **f** were obtained. The structure of these compounds is unambiguously derived from their NMR spectra (Table 1 and 2). Decisive criteria for the individual configurations are of-




| | 28a | 28b | 28c | 28d | 28e | 28f | 28g |
|---|---|---|---|---|---|---|---|
| $R^1$ | Et | H | Et | H | Et | Et | H |
| $R^2$ | Et | Et | Et | Et | H | Et | Et |
| proportion (%) | 12 | 24 | 11 | 19 | 16 | 5 | 13 |

fered by the coupling constants of 2-H and 4-H in the $^1$H-NMR spectra. If one of these protons occupies the *exo* position, its signal shows coupling interactions with 1-H or 5-H (4.1 – 4.6 Hz), respectively, *endo*-3-H (8.5 – 9.0 Hz), and *exo*-3-H (7.6 – 7.9 Hz). In the case of an *endo* position of 2-H and 4-H, the coupling constants with 1-H and 5-H, respectively, and *exo*-3-H are not resolved due to dihedral angles close to 90°, whereas the interaction with *endo*-3-H leads to $J = 4.4 - 5.4$ Hz. These findings are in accord with the boat conformation of the bicyclic ethers, which had been established for the parent hydrocarbon previously[19]. NOE measurements on **28b**, **d**, **e**, **g** corroborate the assignments; in particular, a 6 – 10% effect of the *endo*-6-H signal on saturation of *endo*-3-H and vice versa is good evidence in support of the boat conformation.

In a control experiment, a mixture of **28b**, **f** was exposed to the solvolysis conditions and did not change its composition, indicating that the products **28** do not equilibrate in the reaction mixture. Based on that, the result is best ra-

Table 1. $^1$H-NMR chemical shifts (δ values) and coupling constants of the bicyclo[3.1.0]hexane derivatives **28a–g** in $CDCl_3$

| Compd. | 1-H | 5-H | 2-H | 4-H | *endo*-3-H | *exo*-3-H | *endo*-6-H | *exo*-6-H | $OCH_2$ | $CH_3$ | OH |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **28a** | 1.59 | 1.59 | 4.05 | 4.05 | 1.15 | 2.20 | 0.95 | 0.50 | 3.45, 3.53 | 1.21 | - |
| **28c** | 1.67 | 1.55 | 4.43 | 3.87 | 1.24 | 2.00 | 0.43 - 0.58 | | 3.46, 3.48 (2H), 3.59 | 1.21, 1.22 | - |
| **28f** | 1.68 | 1.68 | 3.84 | 3.84 | 1.44 | 1.88 | - 0.25 | ≈ 0.50 | 3.40 - 3.63 | 1.21 | - |
| **28b** | 1.55 - 1.70 | | 4.41 | 4.04 | 1.10 | 2.23 | 0.93 | 0.50 | 3.44, 3.55 | 1.21 | 1.52 |
| **28d** | 1.45 | 1.70 | 4.28 | 4.48 | 1.35 | 1.91 | 0.45 - 0.57 | | 3.47, 3.59 | 1.22 | 1.59 |
| **28e** | 1.66 | 1.55 | 4.80 | 3.88 | 1.20 | 2.03 | 0.45 - 0.57 | | 3.48 | 1.20 | 1.59 |
| **28g** | 1.58 - 1.71 | | 4.10 | 3.89 | 1.42 | 1.76 | - 0.10 | 0.51 | 3.52 | 1.19 | 2.38 |

$J_{1,endo\text{-}2}$, $J_{endo\text{-}2,\,exo\text{-}3}$, $J_{exo\text{-}3,\,endo\text{-}4}$, and $J_{endo\text{-}4,5}$ were not resolved; $J_{1,\,exo\text{-}2} = J_{exo\text{-}4,\,5} = 4.1$ - 4.6 Hz, $J_{1,5} = 5.7$ Hz, $J_{1,\,endo\text{-}6} = J_{5,\,endo\text{-}6} = 3.7$ - 4.3 Hz, $J_{1,\,exo\text{-}6} = J_{5,\,exo\text{-}6} = 7.7$ - 8.4 Hz, $J_{endo\text{-}2,\,endo\text{-}3} = J_{endo\text{-}3,\,endo\text{-}4} = 4.4$ - 5.4 Hz, $J_{exo\text{-}2,\,endo\text{-}3} = J_{endo\text{-}3,\,exo\text{-}4} = 8.5$ - 9.0 Hz, $J_{exo\text{-}2,\,exo\text{-}3} = J_{exo\text{-}3,\,exo\text{-}4} = 7.6$ - 7.9 Hz, $J_{3,3} = 13.0$ (**28a, b**), 14.5 (**28c, d, e**), 15.5 Hz (**28g, f**), $J_{6,6} = 5.3$ - 5.7 Hz, $J_{2,\,OH} = 6.0$ (**28b**), 11.3 Hz (**28g**); coupling constants in $OCH_2CH_3$ groups: $^2J = 9.1$, $^3J = 7.0$; long range coupling of ≈ 1Hz was observed in several cases for *exo*-3-H and *exo*-6-H, but the coupling partners could not be identified unambiguously.

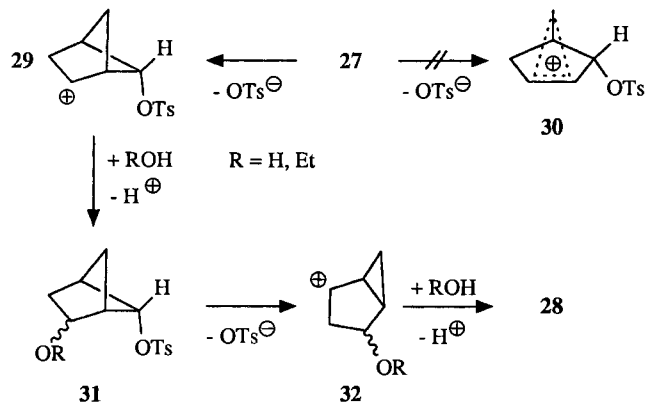



Table 2. $^{13}$C-NMR chemical shifts (δ values) and multiplicities of the signals of the bicyclo[3.1.0]hexane derivatives **28a–g** in $CDCl_3$

| Compd. | C-1 (d) | C-2 (d) | C-3 (t) | C-4 (d) | C-5 (d) | C-6 (t) | $OCH_2$ (t) | $CH_3$ (q) |
|---|---|---|---|---|---|---|---|---|
| **28a** | 19.9 | 77.2 | 31.6 | 77.2 | 19.9 | 2.4 | 64.3 | 15.6 |
| **28c** | 19.5[a] | 79.6[b] | 33.6 | 80.5[b] | 21.8[a] | 4.7 | 63.8<br>64.7 | 15.6[c] |
| **28f** | 22.3 | 80.9 | 34.9 | 80.9 | 22.3 | 5.7 | 63.9 | 15.5 |
| **28b** | 20.4[a] | 70.7 | 34.2 | 77.3 | 22.6[a] | 1.8 | 64.4 | 15.5 |
| **28d** | 19.3[a] | 73.2 | 36.9 | 79.3 | 24.5[a] | 5.1 | 64.8 | 15.6 |
| **28e** | 22.3 | 72.9 | 35.9 | 81.0 | 22.3 | 4.4 | 63.8 | 15.6 |
| **28g** | 20.9[a] | 73.8 | 36.3 | 81.0 | 24.0[a] | 6.7 | 63.8 | 15.5 |

[a, b] These values may be exchanged. - [c] Double intensity.

tionalized by the following mechanism. Heterolysis of one the tosylate bonds of **27** should proceed with simultaneous [1,2] migration with formation of the classical cation **29**, which accepted a nucleophile from both sides, i.e. *trans* as well as *cis* to the tosylated bridge, to give two diastereomeric ethers and alcohols **31**. Also, the leaving of the second tosylate ion required a concomitant [1,2] migration, namely of the methylene group of the four-membered ring. The result would be the classical cations **32** or their isomers with the OR groups next to the cationic centre. The product structures demand that only the former alternative is in operation. Due to the proximity of an electronegative substituent to the developing cationic centre, the latter alternative could be disfavoured. Attack of a nucleophile on the cation **32** would again be possible from two sides resulting in the generation of the compounds **28**. The nonclassical cation **30** is excluded as a dissociation product of **27**, since a nucleophile could be added to it only from the side of the tosylate group. Thus, intermediates **31** with the OR group *trans* to the tosylate group and, in consequence, products **28a**, **b** would not be possible.

## 2. Kinetic Studies

Kinetic data are compiled in Tables 3–6 for solvolyses in various ethanol-water mixtures, and in 60% v/v acetone/water and 97% w/w trifluoroethanol/water. The responses of the solvolyses to variations in solvent-ionizing power were evaluated using the modified Grunwald-Winstein equation (1)[21,23],

$$\lg(k/k_0) = mY_{OTs} \quad (1)$$

where $Y_{OTs}$ is the solvent-ionizing power defined by $m = 1.0$ for solvolyses of 1- or 2-adamantyl tosylates. Solvolyses in which the positive charge is delocalised either by nucleophilic solvent participation ($k_s$ processes) or by neighbouring group participation ($k_\Delta$ processes) usually give $m < 1$[21].

Table 3. Rate constants ($k$) for solvolyses of *cis*-tricyclo-[3.1.0.0$^{2,6}$]hex-3,4-diyl ditosylate (**12**)[a]

| solvent[b] | temp °C | $k$ $s^{-1}$ | $\Delta H^{\neq}$ kcal mol$^{-1}$ | $\Delta S^{\neq}$ eu |
|---|---|---|---|---|
| 80% $C_2H_5OH$ | 25.0 | $1.3 \times 10^{-5}$ [c] | | |
| | 50.0 | $(2.76 \pm 0.04) \times 10^{-4}$ [d] | 22.7 | - 4.6 |
| | 75.0 | $(3.78 \pm 0.01) \times 10^{-3}$ | | |
| 40% $C_2H_5OH$ | 25.0 | $(1.30 \pm 0.01) \times 10^{-4}$ | | |
| 60% $(CH_3)_2C{=}O$[e] | 25.0 | $(1.73 \pm 0.01) \times 10^{-5}$ | | |
| | 55.5 | $(7.46 \pm 0.03) \times 10^{-4}$ | 23.4 | - 1.8 |
| 97% $CF_3CH_2OH$ | 25.0 | $(4.59 \pm 0.05) \times 10^{-5}$ | | |

[a] Determined conductimetrically at least in duplicate with 2,6-lutidine buffer, except where stated otherwise; errors shown are average deviations. - [b] Vol % with water as cosolvent, except for fluorinated alcohols (wt. %). - [c] Calculated from rate constants at other temperatures. - [d] At 50.2 °C, monitoring by HPLC, $k = (2.87 \pm 0.03) \times 10^{-4}$ $s^{-1}$ (based on disappearance of starting ester) and $k = (3.10 \pm 0.05) \times 10^{-4}$ $s^{-1}$ (based on appearance of acid). - [e] Buffered with ethyldiisopropyl amine.

Table 4. Rate constants ($k$) for solvolyses of tricyclo[3.1.0.0$^{2,6}$]hex-3-yl mesylate (**21c**)[a]

| solvent[b] | temp °C | $k$ $s^{-1}$ | $\Delta H^{\neq}$ kcal mol$^{-1}$ | $\Delta S^{\neq}$ eu |
|---|---|---|---|---|
| $C_2H_5OH$ | 25.0 | $(6.40 \pm 0.04) \times 10^{-4}$ | | |
| 80% $C_2H_5OH$ | 25.0 | $(3.53 \pm 0.03) \times 10^{-2}$ | | |
| 40% $C_2H_5OH$ | 0.3 | $(9.51 \pm 0.08) \times 10^{-2}$ | | |
| | 25.0 | $1.59 \pm 0.07$ | 17.9 | 2.5 |
| 60% $(CH_3)_2C{=}O$ | 25.0 | $(6.43 \pm 0.08) \times 10^{-2}$ | | |
| 97% $CF_3CH_2OH$ | 25.0 | $(3.55 \pm 0.35) \times 10^{-1}$ | | |

[a] Determined conductimetrically in duplicate in the presence of triethylamine. - [b] As for Table 3.

Solvolyses involving nucleophilic solvent participation proceed more rapidly in typical aqueous solvolyses (acetone/water or ethanol/water) than in solvolyses in less nucleophilic media [trifluoroethanol (TFE) or carboxylic acids], and the rate ratio for 40% ethanol/water (40E) versus 97% trifluoroethanol/water (97T) (two solvents having almost identical values of $Y_{OTs}$) is a convenient guide to the response to solvent nucleophilicity[21,24].

Solvolyses of bicyclo[2.1.1]hex-2-yl tosylate **25**, which are known (see above) to proceed via competing weak $k_s$ and

Table 5. Rate constants ($k$) for solvolyses of bicyclo[2.1.1]hex-2-yl tosylate (**25**) at 75 °C and *cis*-bicyclo[2.1.1]hex-2,3-diyl ditosylate (**27**) at 125 °C[a]

| | $k$, $s^{-1}$ | | |
|---|---|---|---|
| solvent[b] |  **25**, 75 °C |  **27**, 125 °C | rate ratio |
| 80% $C_2H_5OH$ | $(1.15 \pm 0.01) \times 10^{-4}$ [c] | $(9.4 \pm 0.1) \times 10^{-6}$ [d,e] | 12.2 |
| 60% $C_2H_5OH$ | | $(3.3 \pm 0.4) \times 10^{-5}$ [d] | |
| 40% $C_2H_5OH$ | $(3.79 \pm 0.01) \times 10^{-3}$ | $(9.5 \pm 1) \times 10^{-5}$ [d,f,g] | 39.9 |
| 60% $(CH_3)_2C{=}O$ | | $1.80 \times 10^{-5}$ [f] | |
| 97% $CF_3CH_2OH$ | $(5.47 \pm 0.03) \times 10^{-4}$ | $1.3 \times 10^{-5}$ [f] | 42.1 |
| $HCO_2H$ | $1.5 \times 10^{-2}$ [h] | | |
| $CH_3CO_2H$ | $1.89 \times 10^{-5}$ [i] | | |

[a] Determined conductimetrically in duplicate in the presence of 2,6-lutidine, except where stated otherwise. - [b] As for Table 3. - [c] Additional data at 75 °C, monitoring by HPLC, $k = (1.12 \pm 0.01) \times 10^{-4}$ $s^{-1}$ (based on disappearance of starting ester) and $k = (1.24 \pm 0.02) \times 10^{-4}$ $s^{-1}$ (based on appearance of acid). - [d] Determined by HPLC (based on disappearance of starting ester). - [e] $k = (1.11 \pm 0.03) \times 10^{-5}$ $s^{-1}$ (based on appearance of acid). - [f] Single measurement of rate constant. - [g] Severe technical problems due to low solubility of substrate increased errors. - [h] Calculated from data for the mesylate at lower temperatures (ref. [20]), assuming a tosylate/mesylate rate ratio of 1.0 (ref. [21]). - [i] Data at 74.7 °C from ref. [22]

Table 6. Rate constants ($k$) for solvolyses of tosylates and ditosylates in 80% ethanol/water

| substrate | temp °C | $k$ $s^{-1}$ | $\Delta H^{\neq}$ kcal $mol^{-1}$ | $\Delta S^{\neq}$ eu |
|---|---|---|---|---|
|  **12**[a] | 25.0 | $1.3 \times 10^{-5}$ | 22.7 | - 4.6 |
|  **21d** | 25.0 | $3.4 \times 10^{-2}$ [b] | | |
|  **25** | 25.0 | $2.5 \times 10^{-7}$ [c] | | |
| | 50.2 | $(6.86 \pm 0.24) \times 10^{-4}$ [d] | 24.5 | - 6.5 |
|  **27** | 25.0 | $2 \times 10^{-11}$ [c] | | |
| | 75.0 | $3.8 \times 10^{-8}$ [c] | | |
| | 100.4 | $7.4 \times 10^{-7}$ [e] | 29.5 | - 8.2 |

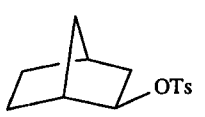
[a] Data from Table 3. - [b] Obtained from rate constant of mesylate (see Table 4), assuming a tosylate/mesylate rate ratio of 0.97 (see ref. [21]). - [c] Calculated from data at other temperatures. - [d] Additional kinetic data from Table 5. - [e] Determined by HPLC, monitoring the disappearance of the starting material (a slightly larger rate constant was obtained from the rate of appearance of acid); additional kinetic data from Table 5.

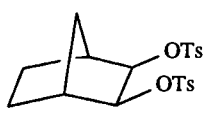
$k_\Delta$ processes[16,25], give a $k_{40E}/k_{97T}$ rate ratio of 6.9 at 75 °C (Table 5). The corresponding ditosylate **27** gives a $k_{40E}/k_{97T}$ rate ratio of 7.3 at 125 °C (Table 5), showing that solvolyses of **25** and **27** have very similar responses to solvent nucleophilicity. Responses to solvent ionizing power ($m$ values, equation 1) are 0.74 ± 0.04 for **25** and 0.52 ± 0.05 for **27** (correlation coefficient $r > 0.99$ for $n = 4$ solvents shown in Table 5 – TFE excluded). Hence, relative rates of these two solvolyses will depend on the solvent ionizing power. In 80% ethanol/water at 25 °C (Table 6), **25** reacts about $1.2 \cdot 10^4$ as fast as **27** (a less highly extrapolated and hence more reliable relative rate at 75 °C is $3.0 \cdot 10^3$).

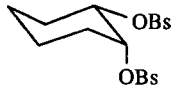
The $k_{40E}/k_{97T}$ rate ratios of 4.5 for solvolyses of the tricyclic mesylate **21c** and of 2.8 for the corresponding ditosylate **12** are even smaller than for solvolyses of **25** and **27** and are similar to the values of 1.76 for 1-adamantyl mesylate and of 1.38 for solvolyses of 2-adamantyl tosylate[21]. An $m$ value of 0.85 ± 0.06 is obtained for solvolyses of **21c** ($r = 0.996$, $n = 4$, Table 4 – TFE excluded), but a lower value of 0.7 was estimated for solvolyses of the tosylate **21d**, using typical tosylate/mesylate rate ratios[21]. The ditosylate **12** gives an $m$ value of 0.53 ± 0.12 ($r = 0.98$, $n = 3$, Table 3 – TFE excluded). These results are consistent with the proposed anchimerically assisted solvolysis mechanism discussed above. Again relative rates will depend on the solvent ionizing power, and in 80% ethanol/water at 25 °C (Table 6) **21d** reacts $2.6 \cdot 10^3$ as fast as **27** (this value agrees with the **25**/**27** rate ratio $3.0 \cdot 10^3$ at 75 °C).

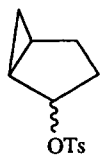
Preliminary kinetic studies of solvolyses of the tricyclic *p*-nitrobenzoate **21b** showed similar solvent effects to solvolyses of the mesylate **21c**, but rate constants in ethanol/water were sensitive to the nature of the buffer (2,6-lutidine or ethyldiisopropylamine). Also, the mesylate/*p*-nitrobenzoate rate ratio was about $10^3$-fold lower than expected from our recent investigations of five secondary and tertiary substrates[5]. Hence, these results support the conclusion from product studies (see above) that solvolyses of **21b** may occur by ring opening prior to dissociation of the carbon leaving group bond.

Relative rates of solvolyses of tosylates and ditosylates (**21d**/**12** and **25**/**27**) are about 100-fold smaller than for acetolyses of *exo*-2-norbornyl tosylate **33** and the corresponding ditosylate **34**[26a], which has been explained by an unavoidable field effect in the rigid norbornyl system[26b]. Our results are similar to the value $1.3 \cdot 10^3$ for acetolyses of the more flexible cyclohexyl brosylate and the corresponding *cis*-1,2-dibrosylate **35**[26c]. Although **12** appears to be at least as rigid as **34**, rearrangement accompanying ionization of **12** may twist the sulfonyl groups out of the most unfavourable orientation. An additional possible explanation of the differences in electron demand is that the developing positive charge may be more highly delocalized in the smaller ring systems **21d** and **25**, so the electron-withdrawing effect of

**33**  

  **34**

**35**  

  **36**

the second sulfonyl group is attenuated[26a]. Comparisons in 80% ethanol/water and further discussion will be presented elsewhere.

Our results (Table 6) show strong anchimeric participation by the bicyclobutane unit in the tricyclic tosylate **21d** and in the corresponding ditosylate **12**, which solvolyse 1.4 · $10^5$ and about 6 · $10^5$ times as fast as **25** and **27**, respectively, in 80% ethanol/water at 25°C. Hence, solvolyses of the bicyclobutyl substrates **21d** and **12** show rate accelerations of about 3 · $10^5$, attributed to the cyclopropylcarbinyl unit. Surprisingly, the extra strain in bicyclobutanes is not manifest as a larger rate enhancement. Approximate kinetic data for acetolyses of bicyclo[3.1.0]hex-2-yl tosylate (**36**)[27], converted using equation (1) to a rate constant of 5 · $10^{-1}$ in 80% ethanol/water at 25°C, suggest that the rigidity introduced by the extra ring in **21d** may actually inhibit 15-fold the ionization of **21d**.

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## Experimental

$^1$H and $^{13}$C NMR: Bruker AC 200, 250, WM 400. — IR: Perkin-Elmer 1420 ratio recording infrared spectrophotometer. — MS: Finnigan MAT 8200. — Elemental analyses: Carlo Erba Strumentatione elemental analyzer 1106. — Melting points: Kofler hot stage from Optische Werke C. Reichert, Vienna, Austria. — Equipment for kinetic studies by conductimetric and HPLC methods were as described previously[5,28].

Solvolysis of the Tricyclic Ditosylate **12** *in the Presence of Ethyldiisopropylamine:* A mixture of **12**[10] (1.50 g, 3.57 mmol), ethyldiisopropylamine (1.38 g, 10.7 mmol), ethanol (30 ml), and water (7.5 ml) was heated under nitrogen at 75°C for 30 min. After cooling, the major quantity of ethanol was removed in vacuo, the residue was saturated with sodium chloride and extracted with ether (3 × 20 ml). The combined ether layers were extracted with saturated sodium chloride solution (50 ml), dried with $MgSO_4$, and concentrated in vacuo. The residue was a yellow-brown liquid (766 mg), which according to the $^1$H-NMR spectrum contained *tricyclo[2.2.0.0$^{2,6}$]hexane-endo-3,endo-5-diol* (**13a**), its monoethyl ether **13b**, and its diethyl ether **13c** in the ratio 1.0:3.9:3.3. Distillation (kugelrohr, 60°C, 0.2–0.02 Torr) gave 453 mg (84%) of **13a**, **b**, **c** in the ratio 1.0:7.8:6.6 in several fractions. The lower boiling fractions were mixtures of **13b** and **c** with different compositions. The dialcohol was identified by comparison of its NMR spectra with published data[10,12].

**13b**: $^1$H NMR ($CDCl_3$): δ = 1.19 (t, $J$ = 7.1 Hz; $CH_3$), 2.14 (m; 1-H), 2.33–2.45 (m; 2,6-H), 2.91 (quint d, $J_{2,4} = J_{3,4} = J_{4,5} = J_{4,6}$ = 4.3, $J_{1,4}$ = 1.0 Hz; 4-H), 3.32–3.63 (m; $CH_2$), 4.17 (dd, $J_{5,6}$ = 2.5 Hz; 5-H), 4.28 (ddd, $J_{3,OH}$ = 11.3, $J_{2,3}$ = 2.4 Hz; 3-H), 4.52 (d; OH; this signal was no longer present, after the sample had been treated with $D_2O$). — $^{13}$C NMR ($CDCl_3$): δ = 10.1 (d; C-1), 15.2 (q; $CH_3$), 24.8 (d; C-6), 28.4 (d; C-2), 48.2 (d; C-4), 63.6 (t; $CH_2$), 69.8 (d; C-3), 75.6 (d; C-5).

**13c**: $^1$H NMR ($CDCl_3$): δ = 1.17 (t, $J$ = 7.0 Hz; $CH_3$), 2.14 (m; 1-H), 2.33–2.45 (m; 2,6-H), 3.00 (quint d, $J_{2,4} = J_{3,4}$ = 4.3, $J_{1,4}$ = 1.2 Hz; 4-H), 3.32–3.63 (m; $CH_2$), 4.06 (m; 3,5-H). — $^{13}$C NMR ($CDCl_3$): δ = 11.4 (d; C-1), 15.2 (q; $CH_3$), 26.2 (d; C-2,6), 48.5 (d; C-4), 63.0 (t; $CH_2$), 73.4 (d; C-3,5).

In an analogous experiment, pure ethanol was used as solvent (4.5 h of refluxing) instead of 80% ethanol/water, and the diether **13c** was obtained in 83% yield.

*Solvolysis of the Tricyclic Ditosylate* **12** *in the Presence of 2,6-Lutidine:* A mixture of **12** (4.00 g, 9.51 mmol), 2,6-lutidine (3.06 g, 28.6 mmol), ethanol (80 ml), and water (20 ml) was heated under nitrogen at 75°C for 30 min and then worked up as in the experiment above. A dark brown oil was obtained which contained *exo-4,exo-6-diethoxybicyclo[3.1.0]hex-2-ene* (**14a**) as the only significant product. By flash chromatography ($SiO_2$, pentane/ethyl acetate, 3:1), **14a** (235 mg, 15%) was isolated as a yellowish liquid.

In a second experiment (300 mg of **12**, 0.71 mmol), after the reaction and the removal of the ethanol the residue was treated with ether (20 ml). The resulting mixture was filtered and the filtrate dried with $Na_2SO_4/Na_2CO_3$. After removal of the ether in vacuo, 100 mg of a red-brown oil remained, which contained **14a** and six aldehydes in the ratio 1.0:1.6. The $^1$H-NMR spectrum showed the signals of the aldehyde functionalities at δ = 9.99, 9.80, 9.78, 9.68, 9.64, and 9.61 in the ratio 2:1:3:3:2:16. Only the least significant component (δ = 9.80) could be identified as *1,3-cyclopentadiene-1-carboxaldehyde* (**15**, see next experiment) by comparison of its spectrum with published data[11b,c]. An attempt to separate the mixture by flash chromatography ($SiO_2$, pentane/ethyl acetate, 3:1) resulted in the isolation of **14a** (10 mg, 12%).

**14a**: MS (70 eV), *m/z* (%): 168 (3) [$M^+$], 123 (26), 103 (53), 95 (32), 94 (37), 75 (66), 67 (40), 66 (72), 65 (58), 47 (100), 45 (62), 39 (39). — $^1$H NMR ($CDCl_3$): δ = 1.19, 1.22 (t, each, $J$ = 7.0 Hz; 2 $CH_3$), 2.00 (dt, $J_{1,5}$ = 6.5, $J_{2,5} = J_{5,6}$ = 1.5 Hz; 5-H), 2.22 (dddd, $J_{1,3}$ = 2.1, $J_{1,2}$ = 1.8, $J_{1,6}$ = 0.9 Hz; 1-H), 2.33 (dd; 6-H), 3.45–3.70 (m; 2 $CH_2$), 4.24 (m; 4-H), 5.60 (ddd, $J_{2,3}$ = 5.5, $J_{3,4}$ = 1.4 Hz; 3-H), 6.09 (dddd, $J_{2,4}$ = 0.6 Hz; 2-H); the assignments are based on NOE measurements. — $^{13}$C NMR ($CDCl_3$): δ = 15.1, 15.6 (q each; 2 $CH_3$), 29.0 (d; C-5), 30.5 (d; C-1), 62.8, 66.2 (t each; 2 $CH_2$), 67.4 (d; C-6), 82.6 (d; C-4), 129.9 (d; C-3), 135.3 (d; C-2); the assignments are based on a $^1$H,$^{13}$C-COSY spectrum.

*Treatment of the Tricyclo[2.2.0.0$^{2,6}$]hexane Derivatives* **13b**, **c** *with Hydrochloric Acid:* A mixture of **13b** (106 mg, 0.76 mmol) and **13c** (75 mg, 0.45 mmol) in ether (50 ml) was shaken vigorously with 2 M HCl (30 ml) in a separatory funnel. The ether layer was separated, dried with $K_2CO_3$, and concentrated in vacuo. A yellow liquid remained (69 mg) which contained **14a**, **15**, *endo-5,anti-6-diethoxybicyclo[2.1.1]hex-2-ene* (**19a**), and *anti-6-ethoxybicyclo[2.1.1]hex-2-en-endo-5-ol* (**19b**) in the ratio 1:4:8:2 and minor quantities of further aldehydes according to the NMR analysis.

**15**: $^1$H NMR ($CDCl_3$): δ = 3.32 (q, $J_{2,5} \approx J_{3,5} \approx J_{4,5} \approx$ 1.4 Hz; 5-$H_2$), 6.71 (ddt, $J_{3,4}$ = 5.2, $J_{2,3}$ = 2.2 Hz; 3-H), 6.90 (d quint, $J_{2,4} \approx$ 1.3 Hz; 4-H), 7.46 (dq; 2-H), 9.80 (d; $J_{4,CHO}$ = 1.1 Hz; CHO), cf. ref.[11b,c] — $^{13}$C NMR ($CDCl_3$): δ = 38.7 (t; C-5), 132.8 (d, double intensity; C-3,4), 142.3 (d; C-2), 149.4 (s; C-1), 186.5 (s; CHO).

**19a**: $^1$H NMR ($CDCl_3$): δ = 1.18, 1.21 (t each, $J$ = 7.0 Hz; 2 $CH_3$), 2.99 (pseudo q; 1,4-H), 3.44, 3.48 (q each; 2 $CH_2$), 4.09 (s; 6-H), 5.24 (t; $J_{1,5}$ = 2.3 Hz; 5-H), 6.60 (pseudo t, $J_{1,2} + J_{1,3}$ = 4.2 Hz; 2,3-H). — $^{13}$C NMR ($CDCl_3$): δ = 15.1, 15.3 (q each; 2 $CH_3$), 54.7 (d; C-1,4), 64.8, 65.8 (t each; 2 $CH_2$), 69.9 (d; C-6), 101.9 (d; C-5), 136.3 (d; C-2,3).

**19b**: $^1$H NMR ($CDCl_3$): δ = 1.21 (t; $J$ = 7.0 Hz; $CH_3$), 3.02 (pseudo q; 1,4-H), 3.48 (q; $CH_2$), 4.10 (s; C-6), 5.48 (br. t, $J_{1,5}$ = 2.2 Hz; 5-H), 6.69 (pseudo t, $J_{1,2} + J_{1,3}$ = 4.2 Hz; 2,3-H); the signal of the OH group could not be located unambiguously. — $^{13}$C NMR ($CDCl_3$): δ = 15.3 (q; $CH_3$), 57.2 (d; C-1,4), 64.8 (t; $CH_2$), 70.1 (d; C-6), 95.5 (d; C-5), 137.3 (d; C-2,3).

*Heating of endo-3,endo-5-Diethoxybicyclo[2.2.0.0$^{2,6}$]hexane* (**13c**) *in 80% Ethanol/Water in the Presence of 2,6-Lutidine/Toluenesulfonic Acid (2:1):* Carried out under the conditions of the solvolysis of ditosylate **12** in the presence of lutidine (see above), this experiment gave the same result as there, i.e. diether **14a** and several aldehydes including **15**.

*7-Oxatetracyclo[4.1.0.0$^{2,4}$.0$^{3,5}$]heptane* (**20**): Different from the previous preparation[10], benzvalene was oxidized with dimethyldioxirane[15]. Under nitrogen, a stirred solution of benzvalene (25.2 mmol) in ether (60 ml) was cooled to −30°C and treated with portions of an anhydrous solution of dimethyldioxirane[15] (19.3 mmol) in acetone (400 ml) in a way that the temperature did not exceed −20°C. After completion of the addition, stirring at about −25°C was continued for 3 h and then the mixture concentrated in vacuo at 0°C. From the residue, the volatile components were evaporated at 20°C/0.01 Torr and condensed in a receiver kept at −78°C. Apart from traces of the solvents, the colourless liquid collected contained 1.12 g (62%) of **20**.

*Tricyclo[3.1.0.0$^{2,6}$]hexan-3-ol* (**21a**): The reduction of epoxide **20** with $LiAlH_4$ in tetrahydrofuran at −50°C according to the published procedure[10] afforded only mixtures of **21a** and tricyclo-[2.2.0.0$^{2,6}$]hexan-3-ol (**22a**). Subsequently, it was found that the reaction gave almost pure **21a** when it was conducted at −30 to −35°C. If the product isolated by distillation or evaporation at 20°C/0.01 Torr and condensation in a receiver kept at −78°C was not pure enough, chromatography (basic $Al_2O_3$ of activity III or IV, pentane/ethyl acetate, 3:1) proved to be useful to provide highly pure **21a**.

*Treatment of a Mixture of the Alcohols* **21a** *and* **22a** *with Sodium Hydride and 4-Nitrobenzoyl Chloride:* A mixture of **21a** (65 mg, 0.68 mmol) and **22a** (46 mg, 0.48 mmol), dissolved in anhydrous tetrahydrofuran (5 ml), was allowed to react with sodium hydride (110 mg, 4.58 mmol), which was added in portions under nitrogen at 0°C. After the mixture had been stirred for 4.5 h at 20°C, 4-nitrobenzoyl chloride (215 mg, 1.16 mmol), dissolved in anhydrous tetrahydrofuran (5 ml), was added dropwise at −15°C within 5 min. Stirring was continued for 30 min at −15°C and for 2.5 h at 20°C. Then a few ml of water and 10 ml of ether were added. Insoluble material was removed by filtration, and the two layers of the filtrate were separated. Drying of the organic layer with $Na_2CO_3/Na_2SO_4$ and concentration in vacuo gave 5 mg (2%) of a yellow oil containing colourless crystals. The $^1$H-NMR spectrum of this crude product showed the presence of *tricyclo[3.1.0.0$^{2,6}$]hex-3-yl* (**21b**), *tricyclo-[2.2.0.0$^{2,6}$]hex-endo-3-yl* (**22b**), and *bicyclo[2.1.1]hex-2-en-exo-5-yl 4-nitrobenzoate* (**23**) in the ratio 2:1:1 as the main components. Traces of **21b** and **23** could be isolated by flash chromatography (basic $Al_2O_3$ of activity III, pentane/ethyl acetate, 10:1), whereas **22b** was lost. The identity of **22b** is based on the characteristic $^1$H-NMR signal ($CDCl_3$) at δ = 5.40 (dd, $J_{3,4}$ = 4.2, $J_{2,3}$ = 2.6 Hz; 3-H). For the data of **21b**, see next experiment.

**23**: $^1$H NMR ($CDCl_3$): δ = 2.44 (dd, $J_{5,syn\text{-}6}$ = 6.8, $J_{6,6}$ = 6.0 Hz; *syn*-6-H), 2.80 (pseudo q; 1,4-H), 3.39 (dt, $J_{1,anti\text{-}6}$ = 2.5 Hz; *anti*-6-H), 5.08 (d; 5-H), 6.84 (pseudo t, $J_{1,2} + J_{1,3}$ = 4.4 Hz; 2,3-H), 8.22−8.35 (m; $C_6H_4$).

*Preparation and Solvolyses of Tricyclo[3.1.0.0$^{2,6}$]hex-3-yl 4-Nitrobenzoate* (**21b**): To an ice-cold solution of alcohol **21a** (1.40 g, 14.6 mmol) in anhydrous pyridine (150 ml) 4-nitrobenzoyl chloride (4.05 g, 21.8 mmol) was added. After having been stirred at 0°C for 7 h, the mixture was kept at 4°C overnight and then poured into ice/water (100 g), which resulted in the precipitation of a beige solid. This material was collected by filtration, dried, and recrystallized from *n*-pentane giving pure **21b** (784 mg, 22%) as colourless crystals, m.p. 85°C.

IR (KBr): $\tilde{\nu}$ = 1709 $cm^{-1}$ (C=O), 1523 ($NO_2$), 1347, 1304, 1278, 740, 721. − $^1$H NMR ($CDCl_3$): δ = 1.39 (≈ dqd, $J_{4,4}$ = 12.3, $J_{1,4} \approx J_{3,4} \approx J_{4,5} \approx$ 1.6, $J_{4,6}$ = 0.8 Hz; *cis*-4-H), 1.97 (≈ dddt, $J_{3,4}$ = 7.3, $J_{4,6} \approx$ 1.6, $J_{1,4} = J_{4,5}$ = 0.7 Hz; *trans*-4-H), 2.09 (≈ dqd, $J_{1,6}$ = 8.9, $J_{1,2} \approx J_{1,5} \approx$ 1.6 Hz; 1-H), 2.12 (m; 5-H), 2.22 (≈ dquint d, $J_{2,6} \approx J_{3,6} \approx J_{5,6} \approx$ 1.6 Hz; 6-H), 2.48 (≈ dq, $J_{2,5}$ = 4.9, $J_{2,3} \approx$ 1.6 Hz; 2-H), 5.19 (≈ dq; 3-H), 8.20, 8.27 (AA'BB spectrum; $C_6H_4$). − $^{13}$C NMR ($CDCl_3$): δ = 3.3 (d; C-6), 5.3 (d; C-1), 31.7 (d; C-5), 34.9 (t; C-4), 37.5 (d; C-2), 79.1 (d; C-3), 123.4 (d; C-3'), 130.7 (d; C-2'), 136.1 (s; C-1'), 150.4 (s; C-4'), 165.0 (s; C=O). − $C_{13}H_{11}NO_4$ (245.2): calcd. C 63.67, H 4.52, N 5.71; found C 64.06, H 4.58, N 5.80.

The solvolyses of **21b** in aqueous acetone and aqueous ethanol required heating at 100°C in a laboratory autoclave for about 2 d and gave complex mixtures. None of the components originating from the tricyclic part of **21b** could be identified. Doublets of triplets in the $^1$H NMR spectrum ($CDCl_3$) at δ = −0.23 and −0.10, respectively, indicated the presence of *cis* disubstituted cyclopropane subunits. In addition, ethyl 4-nitrobenzoate was identified in the case of aqueous ethanol indicating acyl-oxygen cleavage.

*Preparation and Solvolysis of Tricyclo[3.1.0.0$^{2,6}$]hex-3-yl Methanesulfonate* (**21c**): Under nitrogen, a stirred solution of alcohol **21a** (60 mg, 0.62 mmol) and triethylamine (189 mg, 1.87 mmol) in anhydrous dichloromethane (4 ml) was cooled to 0°C. Methanesulfonyl chloride (71.5 mg, 0.62 mmol), dissolved in dichloromethane (1 ml), was added dropwise within 5 min. Stirring was continued for 15 min, and the volatile components were then removed in vacuo at 0°C. NMR spectra of the solution of the residue in $CDCl_3$ were immediately taken under routine conditions.

$^1$H NMR: δ = 1.91 (dddt, $J_{4,4}$ = 12.6, $J_{3,4}$ = 7.2, $J_{4,6}$ = 1.7, $J_{1,4} = J_{4,5}$ = 0.9 Hz; *trans*-4-H), 2.12 (m; 5-H), 2.15 (≈ dqd, $J_{1,6}$ = 8.7, $J_{1,2} \approx J_{1,cis\text{-}4} \approx J_{1,5} \approx$ 1.7 Hz; 1-H), 2.32 (≈ dquint d, $J_{2,6} \approx J_{3,6} \approx J_{5,6} \approx$ 1.7, $J_{cis\text{-}4,6}$ = 1.0 Hz; 6-H), 2.47 (≈ dq, $J_{2,5}$ = 4.9, $J_{2,3}$ = 1.7 Hz; 2-H), 3.04 (s; $CH_3$), 4.94 (≈ dq, $J_{3,cis\text{-}4} \approx$ 1.7 Hz; 3-H); the signal of *cis*-4-H is superimposed by the triplet of $(C_2H_5)_3NH^+$ at 1.38. − $^{13}$C NMR: δ = 2.6 (d; C-6), 4.8 (d; C-1), 30.3 (d; C-5), 34.1 (t; C-4), 37.2 (d; C-2), 37.5 (q; $CH_3$), 83.9 (d; C-3).

The above $CDCl_3$ solution was added to a stirred mixture of acetone (9 ml), water (6 ml), and triethylamine (126 mg, 1.25 mmol) at 20°C. After 5 min of continued stirring, the readily volatile components were removed in vacuo. The residue was saturated with sodium chloride and extracted with ether (4 × 10 ml). The combined ether extracts were washed twice with a saturated aqueous solution of sodium chloride (10 ml each) and dried with $K_2CO_3$. After concentration in vacuo, the remaining colourless liquid consisted mainly of *tricyclo[2.2.0.0$^{2,6}$]hexan-endo-3-ol* (**22a**) as shown by the $^1$H-[10] and $^{13}$C-NMR spectra[12].

*Bicyclo[2.1.1]hex-2-yl p-Toluenesulfonate* (**25**) has been mentioned in the literature[16a,20], but no data are described. We have prepared **25** from bicyclo[2.1.1]hexan-2-ol[16b] under routine conditions (see next experiment). The workup afforded **25** as an oily liquid which solidified at −20°C to give colourless crystals in 48% yield, m.p. 33−35°C.

$^1$H NMR ($CDCl_3$): δ = 0.87, 1.39 (dd each, $J_{5,6}$ = 9.9, $J_{5,5} = J_{6,6}$ = 7.3 Hz; *endo*-5,*syn*-6-H), 1.53 (ddt, $J_{3,3}$ = 12.0, $J_{3,anti\text{-}6}$ = 3.9, $J_{2,3} = J_{3,4}$ = 1.7 Hz; *cis*-3-H), 1.59−1.66 (m; *exo*-5,*anti*-6-H), 1.96 (dddd, $J_{2,3}$ = 7.3, $J_{3,anti\text{-}5}$ = 2.5, $J_{3,4}$ = 1.4 Hz; *trans*-3-H), 2.38 (dtt, $J_{1,4}$ = 6.4, $J_{4,exo\text{-}5} = J_{4,anti\text{-}6}$ = 2.9 Hz; 4-H), 2.42 (s; $CH_3$), 2.53 (dq, $J_{1,2} = J_{1,exo\text{-}5} = J_{1,anti\text{-}6}$ = 2.5 Hz; 1-H), 4.96 (dq, $J_{2,exo\text{-}5}$ = 1.4 Hz; 2-H), 7.32, 7.78 (AA'XX' spectrum; $C_6H_4$). − $^{13}$C-NMR ($CDCl_3$): δ = 21.6 (q; $CH_3$), 35.7, 35.8, 38.4 (t each; C-3,5,6), 38.4 (d; C-4), 44.8 (d; C-1), 82.9 (d; C-2), 127.7, 129.8 (d each; C-2',3'), 134.6, 144.5 (s each; C-1',4').

*cis-Bicyclo[2.1.1]hex-2,3-diyl Bis(p-toluenesulfonate)* (**27**): A stirred solution of *cis*-bicyclo[2.1.1]hexane-2,3-diol[17,18] (1.75 g, 15.3 mmol) in pyridine (50 ml) kept at 0°C and under nitrogen was treated with *p*-toluenesulfonyl chloride (6.56 g, 34.4 mmol), which was added cautiously in several portions. After additional stirring for 5 h at 0°C, the mixture was kept for 2 d at 4°C and then poured into ice/water (190 g). Hydrochloric acid (125 ml 2 M) was added and the mixture extracted with dichloromethane (3 × 75 ml). The combined organic layers were washed with hydrochloric acid (50

ml 2 M), saturated aqueous $Na_2CO_3$ solution (50 ml), and finally with water (50 ml). After drying with $Na_2SO_4$ and concentration in vacuo, the dichloromethane solution left a yellow oil which was dissolved in a few ml of ethanol. Cooling at 4°C resulted in the precipitation of pure **27** (3.32 g, 51%), m.p. 96–99°C.

MS (70 eV), *m/z* (%): 422 (0.6) [$M^+$], 267 (7), 157 (5), 156 (9), 155 (100), 139 (5), 92 (8), 91 (78), 67 (6), 65 (14). – $^1$H NMR ($CDCl_3$): δ = 0.81 (dd, $J_{endo\text{-}5,syn\text{-}6}$ = 9.5, $J_{6,6}$ = 8.7 Hz; *syn*-6-H), 1.70 (dt, $J_{1,anti\text{-}6}$ = 3.5 Hz; *anti*-6-H), 1.73 (br. dt, $J_{5,5}$ = 8.0, $J_{1,exo\text{-}5} \approx$ 2.0 Hz; *exo*-5-H), 1.79 (dd; *endo*-5-H), 2.45 (s; $CH_3$), 2.55 (br. t; 1,4-H), 4.86 (br. s; 2,3-H), 7.33, 7.79 (AA'XX' spectrum; $C_6H_4$). – $^{13}$C NMR ($CDCl_3$): δ = 21.7 (q; $CH_3$), 32.6, 32.8 (t each; C-5,6), 43.7 (d; C-1,4), 77.6 (d; C-2,3), 127.9, 129.8 (d each; C-2′,3′), 133.6, 144.8 (s each; C-1′,4′). – $C_{20}H_{22}O_6S_2$ (422.5): calcd. C 56.85, H 5.25; found C 56.22, H 5.49.

*Solvolysis of Ditosylate* **27**: A mixture of **27** (959 mg, 2.27 mmol), ethyldiisopropylamine (1.18 g, 9.31 mmol), ethanol (32 ml), and water (8 ml) was heated at 130°C for 141 h in a laboratory autoclave, whereupon the ethanol was evaporated in vacuo at 20°C. The residue was saturated with sodium chloride and extracted with ether (3 × 25 ml). The combined ether layers were dried with $Na_2SO_4$ and concentrated in vacuo to give a brown liquid (456 mg), which was subjected to flash chromatograhy ($SiO_2$, gradient elution with pentane/ethyl acetate from 2:1 to pure ethyl acetate). The following fractions were obtained as colourless liquids (in order of elution): (i) *endo,endo*-(**28a**), *endo,exo*-(**28c**), and *exo,exo-2,4-diethoxybicyclo[3.1.0]hexane* (**28f**) in the ratio 12:11:5 (74 mg, 20% yield); (ii) *exo-4-ethoxybicyclo[3.1.0]hexan-2-exo-ol* (**28g**, 29 mg, 9%); (iii) *endo-4-ethoxybicyclo[3.1.0]hexan-endo-2-ol* (**28b**), *endo-4-ethoxybicyclo[3.1.0]hexan-exo-2-ol* (**28d**), and *exo-4-ethoxybicyclo-[3.1.0]hexan-endo-2-ol* (**28e**) in the ratio 24:19:16 (136 mg, 42%).

The ratios of the products were determined by $^1$H-NMR spectroscopy (cf. Table 1). Almost complete assignments were possible after further separations by preparative gas chromatography (Carlo Erba Strumentatione GC 6000, Vega Series 2; length of column: 3 m; 25% Carbowax 20 M on Chromosorb A). Accordingly, small quantities of almost pure **28a** (column temperature 90°C, slower elution), **28c** (faster elution), and **28b** (column temperature 125°C, slower elution) as well as a mixture of **28d** and **28e** (faster elution) in the ratio 2:1 were obtained.

The $^{13}$C-NMR chemical shifts of all compounds **28** are collected in Table 2. The analysis of the spectrum of the crude product resulted in a product distribution very similar to that given in the formula scheme. Additional signals at δ = 6.8, 24.2, 40.0, and 73.6 may be evidence for *bicyclo[3.1.0]hexane-exo-2,exo-4-diol*, which would have been present in a quantity about equal to that of **28c**. The other diols (*endo,endo* and *endo,exo*) may have remained in the aqueous phase.

MS (70 eV) of **28b**, *m/z* (%): 142 (0.1) [$M^+$], 101 (38), 88 (39), 85 (30), 79 (23), 73 (37), 72 (67), 70 (23), 69 (20), 67 (44), 57 (100), 55 (20), 43 (43), 41 (51), 39 (28).

*Kinetics:* Conventional conductimetric procedures[28a] were employed for solvolyses of the tricyclic ditosylate **12** and the tosylate **25**, and the fast-response conductimetric method for unstable mesylates[28b] was applied to solvolyses of the tricyclic mesylate **21c**. HPLC analyses for solvolyses of tosylate **25** and ditosylates **12** and **27** were as described previously[28c].

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* Dedicated to Professor *John D. Roberts* on the occasion of his 75th birthday.

[1] [1a] J. D. Roberts, R. H. Mazur, *J. Am. Chem. Soc.* **1951**, *73*, 2509–2520, 3542–3543. – [1b] K. B. Wiberg, B. A. Hess, Jr., A. J. Ashe, III in *Carbonium Ions* (Eds.: G. A. Olah, P. v. R. Schleyer), Wiley, New York, **1972**, vol. III, chapter 26. – [1c] E. C. Friedrich in *The Chemistry of the Cyclopropyl Group* (Eds.: S. Patai, Z. Rappoport), Wiley, Chichester, **1987**, Part I, chapter 11.

[2] H. C. Brown, E. N. Peters, *J. Am. Chem. Soc.* **1977**, *99*, 1712–1716.

[3] R. Breslow, H. Bozimo, P. Wolf, *Tetrahedron Lett.* **1970**, 2395–2397.

[4] S. Masamune, K. Fukumoto, Y. Yasunari, D. Darwish, *Tetrahedron Lett.* **1966**, 193–200.

[5] T. W. Bentley, M. Christl, S. J. Norman, *J. Org. Chem.* **1991**, *56*, 6238–6240.

[6] S. Masamune, M. Sakai, H. Ona, *J. Am. Chem. Soc.* **1972**, *94*, 8955–8956.

[7] W.-D. Stohrer, R. Hoffmann, *J. Am. Chem. Soc.* **1972**, *94*, 1661–1668.

[8] S. Masamune, M. Sakai, H. Ona, A. J. Jones, *J. Am. Chem. Soc.* **1972**, *94*, 8956–8958; V. I. Minkin, N. S. Zefirov, M. S. Korobov, N. V. Averina, A. M. Boganov, L. E. Nivorozhkin, *Zh. Org. Khim.* **1981**, *17*, 2616–2618; *Chem. Abstr.* **1982**, *96*, 142155k; G. Maier, H. Rang, H.-O. Kalinowski, *Angew. Chem.* **1989**, *101*, 1293–1295; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1232.

[9] K. Yano, K. Yoshida, *J. Org. Chem.* **1977**, *42*, 363–365.

[10] M. Christl, H. Leininger, P. Kemmer, *Chem. Ber.* **1984**, *117*, 2963–2987; in procedure b) for the synthesis of the *cis*-glycol, from which **12** is prepared, $(C_2H_5)_4N^+Cl^-$ should be replaced by $(C_2H_5)_4N^+OH^-$.

[11] [11a] K. Hafner, G. Schulz, K. Wagner, *Liebigs Ann. Chem.* **1964**, *678*, 39–53. – [11b] L. Kaplan, L. A. Wendling, K. E. Wilzbach, *J. Am. Chem. Soc.* **1971**, *93*, 3819–3820. – [11c] T. Okuyama, Y. Ikenouchi, T. Fueno, *J. Am. Chem. Soc.* **1978**, *100*, 6162–6166.

[12] M. Christl, H. Leininger, B. Mattauch, *Spectrosc. Int. J.* **1983**, *2*, 184–189.

[13] [13a] F. T. Bond, L. Scerbo, *Tetrahedron Lett.* **1968**, 2789–2792; W. R. Roth, A. Friedrich, *ibid.* **1969**, 2607–2610; H. M. Frey, R. G. Hopkins, *J. Chem. Soc. B* **1970**, 1410–1412; F. Scheidt, W. Kirmse, *J. Chem. Soc., Chem. Commun.* **1972**, 716. – [13b] R. J. Roth, T. J. Katz, *J. Org. Chem.* **1980**, *45*, 961–965.

[14] D. H. Gibson, C. H. DePuy, *Chem. Rev.* **1974**, *74*, 605–623.

[15] W. Adam, R. Curci, J. O. Edwards, *Acc. Chem. Res.* **1989**, *22*, 205–211; W. Adam, L. Hadjiarapoglou, A. Smerz, *Chem. Ber.* **1991**, *124*, 227–232; W. Adam, J. Bialas, L. Hadjiarapoglou, *ibid.* **1991**, *124*, 2377.

[16] [16a] G. Seybold, P. Vogel, M. Saunders, K. B. Wiberg, *J. Am. Chem. Soc.* **1973**, *95*, 2045–2047. – [16b] W. Kirmse, V. Zellmer, B. Goer, *J. Am. Chem. Soc.* **1986**, *108*, 4912–4917.

[17] W. Trautmann, H. Musso, *Chem. Ber.* **1981**, *114*, 982–989.

[18] M. Christl, A. Kraft, *Angew. Chem.* **1988**, *100*, 1427–1428; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1369–1370.

[19] R. L. Cook, T. B. Malloy, Jr., *J. Am. Chem. Soc.* **1974**, *96*, 1703–1707; M. Christl, *Chem. Ber.* **1975**, *108*, 2781–2791.

[20] E. W. Della, G. M. Elsey, G. Skouroumounis, *Aust. J. Chem.* **1990**, *43*, 1231–1244.

[21] T. W. Bentley, G. Llewellyn, *Prog. Phys. Org. Chem.* **1990**, *17*, 121–158.

[22] J. Meinwald, J. C. Shelton, G. L. Buchanan, A. Courtin, *J. Org. Chem.* **1968**, *33*, 99–105.

[23] E. Grunwald, S. Winstein, *J. Am. Chem. Soc.* **1948**, *70*, 846–854.

[24] D. J. Raber, W. C. Neal, Jr., M. D. Dukes, J. M. Harris, D. L. Mount, *J. Am. Chem. Soc.* **1978**, *100*, 8137–8146.

[25] [25a] T. W. Bentley, B. Goer, W. Kirmse, *J. Org. Chem.* **1988**, *53* 3066–3073. – [25b] P. v. R. Schleyer, K. Laidig, K. B. Wiberg, M. Saunders, M. Schindler, *J. Am. Chem. Soc.* **1988**, *110*, 300–301. – [25c] L. R. Schmitz, T. S. Sorensen, *J. Am. Chem. Soc.* **1980**, *102*, 1645–1648.

[26] [26a] J. B. Lambert, A. G. Holcomb, *J. Am. Chem. Soc.* **1971**, *93*, 2994–3001. – [26b] D. C. Kleinfelter, J. M. Miller, Jr., *J. Org. Chem.* **1973**, *38*, 4142–4147. – [26c] S. Winstein, E. Grunwald, L. L. Ingraham, *J. Am. Chem. Soc.* **1948**, *70*, 821–828.

[27] E. C. Friedrich, M. A. Saleh, S. Winstein, *J. Org. Chem.* **1973**, *38*, 860–864; see also, E. C. Friedrich, M. A. Saleh, *J. Am. Chem. Soc.* **1973**, *95*, 2617–2623.

[28] [28a] T. W. Bentley, C. T. Bowen, D. H. Morten, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1981**, *103*, 5466–5475. – [28b] T. W. Bentley, W. Kirmse, G. Llewellyn, F. Söllenböhmer, *J. Org. Chem.* **1990**, *55*, 1536–1540. – [28c] T. W. Bentley, G. E. Gream, *J. Org. Chem.* **1985**, *50*, 1776–1778.

[94/93]