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Unsubstituted Bicyclo[1.1.0]but-2-ylcarbinyl Cations

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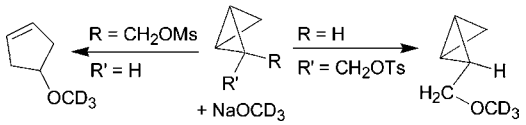

A synthesis for the unsubstituted bicyclo[1.1.0]but-2-ylmethanols (*endo*- and *exo*-**9**) from 1,3-butadiene has been developed. Solvolyses of their sulfonates **10** and **11** took entirely different courses, as the endo compound **10** gave rise exclusively to rearranged products such as cyclopent-3-en-1-ol (**14**), while the exo compound **11** underwent only the substitution of the tosylate group with complete retention of the *exo*-bicyclo[1.1.0]but-2-ylmethyl skeleton. Under solvolytic conditions, **10** reacted at very similar rates to the corresponding monocyclic substrate, that is, cyclopropylcarbinyl mesylate (**19**); in contrast, **11** reacted only three times as fast as *n*-butyl tosylate and about 1000-fold slower than **10**. The nature of the bicyclo[1.1.0]but-2-ylcarbinyl cations has been probed by quantum chemical calculations. Whereas, the exo isomer (*exo*-**18**) corresponds to a local energy minimum, the endo isomer is only a transition state [*endo*-**18(TS)**] for an automerization of the nonclassical cyclopent-3-en-1-yl cation (**13**) and converts into **13** by a Wagner−Meerwein rearrangement. The most favorable isomerization of *exo*-**18** also leads to **13** but via a transition state resembling the 2-vinylcycloprop-1-yl cation [**25(TS)**]. On the introduction of methyl groups at positions 1 and 3 of *exo*-**18**, the cation is no longer an energy minimum and it becomes a transition state [**27(TS)**] for an automerization of the nonclassical 1,3-dimethylcyclopent-3-en-1-yl cation (**28**). The large effect of the methyl substitution rationalizes the puzzling results of the previous product and rate studies, which utilized various substituted derivatives of bicyclo[1.1.0]but-2-ylcarbinyl sulfonates as substrates.

Introduction

In 1970, Breslow et al.[1] published a communication entitled "Bicyclo[1.1.0]butyl-2-carbinyl Cations" and reported rate constants of the solvolysis of the di- and trisubstituted bicyclo-[1.1.0]but-2-ylcarbinyl tosylates **1** and **2** (Scheme 1). Whereas no product structures were given in the case of **1**, the cyclopentenol **3** was described as the major compound formed from both *endo*-**2** and *exo*-**2** on hydrolysis in 80% (v/v) dioxane/water with an exo/endo rate ratio of 2 (the rate constants at 25 °C being 2.71×10^{-4} and 5.63×10^{-4} s^{-1}, respectively).

After having investigated a number of endo,endo-bridged bicyclo[1.1.0]but-2-ylcarbinyl esters, that is, tricyclo[3.1.0.$0^{2,6}$]-hex-3-yl sulfonates[2] and tricyclo[4.1.0.$0^{2,7}$]hept-3-yl, as well as -hept-4-en-3-yl esters,[3] we studied the solvolysis of monosubstituted bicyclo[1.1.0]but-2-ylcarbinyl esters [dimesylates *endo*,*endo*- and *exo*,*exo*-**4** (Scheme 2)][4] and found substantial differences on comparison with the results for the diastereoisomers of **2**. As expected, *endo*,*endo*-**4** gave rise exclusively to rearranged solvolysis products such as **5**, but no rearrangement occurred in the case of *exo*,*exo*-**4**, as illustrated by the formation of the ethyl ether **6**. Furthermore, *endo*,*endo*-**4** underwent hydrolysis in 40% (v/v) acetone/water at 25 °C about eight times as fast as *exo*,*exo*-**4**, that is, the exo/endo rate was <1, despite the deactivating effect on the endo substrate of the second CH_2OMs group in close proximity.[4]

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(1) Breslow, R.; Bozimo, H.; Wolf, P. *Tetrahedron Lett.* **1970**, 2395−2397.
(2) Bentley, T. W.; Norman, S. J.; Gerstner, E.; Kemmer, R.; Christl, M. *Chem. Ber.* **1993**, *126*, 1749−1757.
(3) Bentley, T. W.; Llewellyn, G.; Norman, S. J.; Kemmer, R.; Kunz, U.; Christl, M. *Liebigs Ann./Recl.* **1997**, 229−244.

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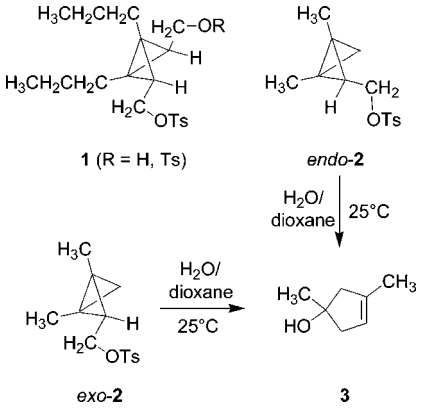
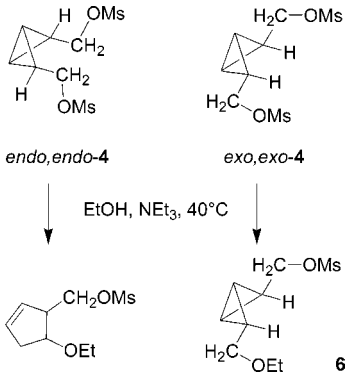
SCHEME 1. Bicyclo[1.1.0]butyl-2-carbinyl Tosylates Solvolyzed by Breslow et al.[1]



SCHEME 2. Ethanolysis of the Bicyclo[1.1.0]butan-2,4-dimethanol Dimesylates *endo,endo*-4 and *exo,exo*-4[4]

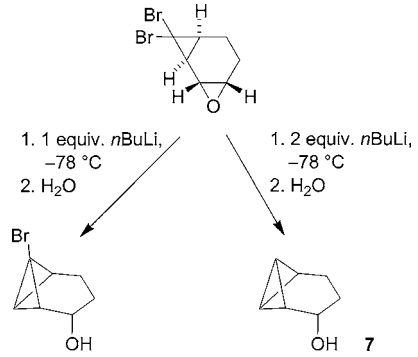


To understand the differences between system **2** and system **4** regarding the rates as well as the effect of substituents on the mechanism of the solvolysis reactions, we now report the first investigation of the parent systems, namely, the unsubstituted diastereomeric bicyclo[1.1.0]but-2-ylcarbinyl sulfonates, by experimental methods and the corresponding bicyclo[1.1.0]but-2-ylcarbinyl cations by quantum chemical calculations.

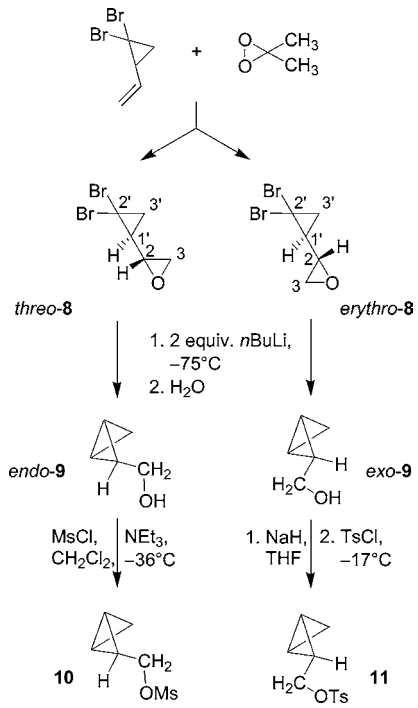
Results and Discussion

1. Synthesis of *endo*-Bicyclo[1.1.0]but-2-ylcarbinyl Mesylate (10) and *exo*-Bicyclo[1.1.0]but-2-ylcarbinyl Tosylate (11). *endo*- (*endo*-9) and *exo*-Bicyclo[1.1.0]butane-2-methanol (*exo*-9). On the basis of the observations of Coates et al.,[5] who obtained homocyclopropylcarbinols by reductive cyclization of bromocyclopropyl epoxides, Tischer[6] developed the most efficient one among the syntheses of tricyclo[4.1.0.0^{2,7}]heptan-3-ol (**7**),[3] which is depicted in Scheme 3. We applied this reaction sequence to the preparation of both bicyclo[1.1.0]-butane-2-methanols **9** (Scheme 4). Accordingly, the known 1,1-dibromo-2-vinylcyclopropane[7] was treated with dimethyldioxirane, which is the epoxidation reagent of choice with regard to the purity of the products.[8] The resulting 1:1 mixture of the epoxides **8** was separated by chromatography, and the assignment of their configuration was deduced from the outcome of their reaction with 2 equivalents of *n*-butyllithium. It is assumed that the anionic carbon atoms of the carbenoids formed from the **8** isomers attack the epoxide subunits in an S_N2-type manner, which is why we take *threo*-**8** as the precursor of *endo*-bicyclo-[1.1.0]butane-2-methanol (*endo*-**9**) and *erythro*-**8** as the precursor of *exo*-**9**. Both alcohols **9** were obtained as colorless liquids, from which an impurity of 1-butanol could not be removed completely as a result of the sensitivity of the compounds. The presence of the bicyclo[1.1.0]butane moieties in the products emerging from **8** was derived from typical NMR data such as $\delta = 1.7$ and -0.3 for C1,3 as well as $J_{C1,H1} = J_{C3,H3} = 201.3$ and 203.7 Hz for *endo*-**9** and *exo*-**9**, respectively. The stereochemical assignment is unambiguous on the basis of the

SCHEME 3. Synthesis of Tricyclo[4.1.0.0^{2,7}]heptan-3-ol (7) According to Tischer[6]



SCHEME 4. Syntheses of *endo*-Bicyclo[1.1.0]but-2-ylcarbinyl Mesylate (10) and *exo*-Bicyclo[1.1.0]but-2-ylcarbinyl Tosylate (11)



(4) Bentley, T. W.; Llewellyn, G.; Kottke, T.; Stalke, D.; Cohrs, C.; Herberth, E.; Kunz, U.; Christl, M. *Eur. J. Org. Chem.* **2001**, 1279−1292.

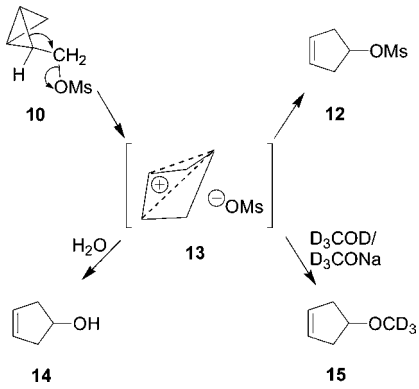
(5) (a) Last, L. A.; Fretz, E. R.; Coates, R. M. *J. Org. Chem.* **1982**, *47*, 3211−3219. (b) Coates, R. M.; Last, L. A. *J. Am. Chem. Soc.* **1983**, *105*, 7322−7326.

(6) Tischer, W. Dissertation, Universität München, Germany, 1991.

(7) (a) Skell, P. S.; Garner, A. Y. *J. Am. Chem. Soc.* **1956**, *78*, 5430−5433. (b) Huwyler, R.; Al-Dulayymi, A.; Neuenschwander, M. *Helv. Chim. Acta* **1999**, *82*, 2336−2347.

(8) Adam, W.; Saha-Möller, C. R.; Zhao, C.-G. *Org. React.* **2002**, *61*, 219−516.

SCHEME 5. Solvolysis Products of *endo*-Bicyclo[1.1.0]but-2-ylcarbinyl Mesylate (10)



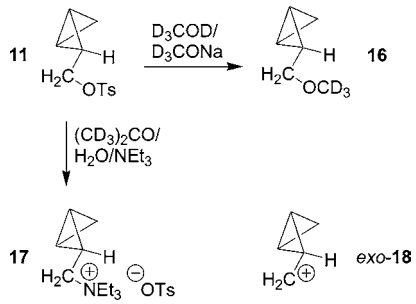
following characteristic coupling constants: $J_{1,2} = J_{2,3} = 3.3$ Hz for *endo*-**9** and 0.9 Hz for *exo*-**9**; $J_{C2,H2} = 150.7$ Hz for *endo*-**9** and about 170 Hz for *exo*-**9**.

Conversion of the Alcohols 9 into the Sulfonates 10 and 11. With regard to the preparation of sulfonates from the alcohols **9**, we anticipated the same difficulties as experienced previously in the case of related compounds.[2,3] Thus, a mixture of *endo*-**9** and triethylamine in $CDCl_3$ was treated with methanesulfonyl chloride at −36 °C. The desired mesylate **10** could be observed by NMR spectroscopy of the reaction mixture without workup. However, the persistence of **10** was found to be limited. On standing at room temperature for a day, 40% of the amount of **10** in the NMR sample converted into cyclopent-3-en-1-yl mesylate (**12**) and a second 4-substituted cyclopentene in the ratio of 2:1. Whereas **12** was the product of the internal return of the ion pair from **13** and the mesylate ion formed in the heterolytic dissociation of **10** (Scheme 5), the second product resulted from the collapse of **13** with another nucleophile of the sample, for example, triethylamine, chloride, or unintentionally present water. The consumption of **10** was complete after 9 days at room temperature.

An analogous experiment to prepare the mesylate of *exo*-**9** failed, most probably because of the acidification of the mixture brought about by the formation of triethylammonium chloride, which is supposed to catalyze irreversible reactions of the bicyclo[1.1.0]butane system of *exo*-**9** and possibly its mesylate as well. We then turned to a method that avoids acids entirely and, thus, deprotonated *exo*-**9** with sodium hydride prior to the addition of tosyl chloride to the reaction mixture. Indeed, the desired tosylate **11** was produced and obtained as a 4:1 mixture with 1-butyl tosylate after the workup. At variance with the behavior of **10**, an NMR sample of **11** remained unchanged at room temperature. The identity of the sulfonates **10** and **11** was clearly established by their NMR spectra. Whereas the multiplicities of the signals were very similar to those of the alcohols **9**, several chemical shifts showed the typical changes expected for the conversion of an alcohol into its sulfonate.[3,4]

2. Solvolysis of *endo*-Bicyclo[1.1.0]but-2-ylcarbinyl Mesylate (10) and *exo*-Bicyclo[1.1.0]but-2-ylcarbinyl Tosylate (11). Product Studies. As the thermal rearrangement of **10** to cyclopent-3-en-1-yl mesylate (**12**) already indicated, the heterolytic dissociation of **10** gives rise to the cation **13** (Scheme 5). This was confirmed by the dissolution of **10** in 75% acetone/water as well as in [D_4]methanol containing sodium [D_3]-methoxide at room temperature. In both cases, **12** emerged as one of the products, while the second was cyclopent-3-en-1-ol (**14**) and cyclopent-3-en-1-yl [D_3]methyl ether (**15**), respectively.

SCHEME 6. Solvolysis Products of *exo*-Bicyclo[1.1.0]but-2-ylcarbinyl Tosylate (11)



Scheme 5 illustrates the mechanism in which the reorganization of the skeleton of **10** should proceed simultaneously with the cleavage of the C−O bond. This view is supported by the complete absence of the unrearranged products.

The solvolysis of **11** took an entirely different course, as only products with a retained carbon atom skeleton were observed. Thus, on dissolution in [D_4]methanol containing sodium [D_3]-methoxide at room temperature, **11** was converted into *exo*-bicyclo[1.1.0]but-2-ylcarbinyl [D_3]methyl ether (**16**) in good yield (Scheme 6).

Attempts to attain a hydrolysis product of **11** were to no avail. Whereas the consumption of **11** in aqueous acetone of various concentrations in the presence of sodium bicarbonate or triethylamine seemed to proceed surprisingly slowly, a product could not be identified. The monitoring by NMR spectroscopy of the fate of **11** in 90% aqueous [D_6]acetone containing triethylamine then revealed the formation of (*exo*-bicyclo[1.1.0]-but-2-ylcarbinyl)triethylammonium tosylate (**17**; Scheme 6). At room temperature, **11** was consumed to the extent of 71% within 118 days, with the yield of **17** amounting to 41%. The identity of **17** was determined on the basis of the similarity of its NMR spectroscopic data with those of **11** and, in particular, by the highly characteristic splitting of certain signals as a result of the scalar coupling of the respective nuclei with the ^{14}N nucleus.[9]

Being present as an impurity, 1-butyl tosylate underwent analogous reactions as **11**, that is, it was transformed to 1-butyl [D_3]methyl ether and 1-butyltriethylammonium tosylate, respectively. Throughout these reactions, the ratio of the concentrations of **11** and 1-butyl tosylate remained constant. In the case of the methanolysis, a variation of the reaction rate was qualitatively observed when different concentrations of the substrates were utilized. These findings are in line with S_N2 processes for solvolyses of **11** and at variance with the intermediacy of the *exo*-bicyclo[1.1.0]but-2-ylcarbinyl cation (*exo*-**18**; Scheme 6).

In summary, the products **12**, **14**, and **15** on one hand and **16** and **17** on the other are in harmony with the results of the solvolyses of *endo*,*endo*- and *exo*,*exo*-**4** (Scheme 2) and emphasize the discrepancy between them and the formation of the common product **3** on the solvolysis of *endo*- and *exo*-**2** (Scheme 1).

Kinetic Studies. Rate constants were obtained for the solvolyses in methanol (Table 1) and acetone/water (Table 2). A scaled-down procedure for the in situ preparation of mesylates was tested for the known solvolyses of 1-adamantyl mesylate in methanol (monitored conductometrically).[10] The method is

(9) Berger, S.; Braun, S.; Kalinowski, H.-O. NMR-Spektroskopie von Nichtmetallen. *^{15}N NMR-Spektroskopie*, Band 2; Georg Thieme Verlag: Stuttgart, 1992.

TABLE 1. Rate Constants (*k*) for Solvolyses of Sulfonates in Methanol Containing Triethylamine

substrate	*T* (°C)	NEt_3 (M)	*k* (s^{-1})
1-AdOMs[a,b]	25.0	*c*	$(2.71 \pm 0.02) \times 10^{-4}$
endo-OMs (**10**)	25.0	*c*	$(1.42 \pm 0.04) \times 10^{-4}$
endo-OMs (**10**)[d,e]	40.0	*c*	$(8.65 \pm 0.17) \times 10^{-4}$
endo-OMs (**10**)	40.0	0.01	$(8.72 \pm 0.09) \times 10^{-4}$
exo-OTs (**11**)[f]	40.0	0.01	$(2.95 \pm 0.2) \times 10^{-6}$
1-BuOTs[g]	40.0	0.01	$(1.11 \pm 0.08) \times 10^{-6}$
exo-OTs (**11**)[g]	40.0	0.003	$(3.32 \pm 0.13) \times 10^{-6}$
1-BuOTs[g]	40.0	0.003	$(1.08 \pm 0.02) \times 10^{-6}$
exo-OTs (**11**)[h,i]	25.0		$\approx 6.0 \times 10^{-7}$

[a] Determined conductometrically in duplicate; errors shown are average deviations. [b] Reference 10: $k = (2.81 \pm 0.02) \times 10^{-4}$. [c] The solution contained a small excess of triethylamine, carried through from the in situ preparation of the mesylate. [d] Determined conductometrically in triplicate. [e] Activation parameters: $\Delta H^{\ddagger} = 21.8$ kcal mol^{-1}; $\Delta S^{\ddagger} = -3.2$ cal mol^{-1} K^{-1}. [f] The rate constant is an average of one conductometric and one kinetic run monitored by HPLC. [g] The rate constant was obtained from one HPLC kinetic run for a mixture of 1-butyl tosylate and **11**. [h] Estimated from data at 40 °C, assuming $\Delta S^{\ddagger} = -20$ cal mol^{-1} K^{-1} (for an S_N2 alcoholysis of a benzenesulfonate, see ref 12). [i] Two reactions monitored by ^1H NMR (see experimental) at 22 °C in the presence of about 0.3 M methoxide gave higher rate constants (approximate half-lives were 9−24 h, corresponding to $k \approx 10^{-5}$ s^{-1}).

TABLE 2. Rate Constants (*k*) for Solvolyses of Sulfonates in Acetone/Water (% v/v) Containing Triethylamine at 25.0 °C

substrate	% v/v	NEt_3 (M)	*k* (s^{-1})
endo-OMs (**10**)[a]	60	*b*	$(1.75 \pm 0.04) \times 10^{-3}$
endo-OMs (**10**)[a,c]	40	*b*	$(1.00 \pm 0.03) \times 10^{-2}$
exo-OTs (**11**)[d]	60	0.003	$(4.82 \pm 0.12) \times 10^{-7}$
1-BuOTs[d]	60	0.003	$(1.62 \pm 0.06) \times 10^{-7}$

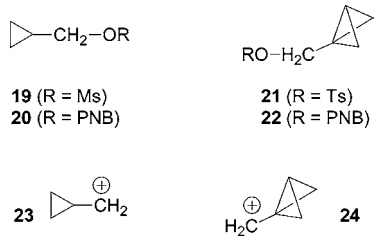
[a] Refer to Table 1, footnote a. [b] Refer to Table 1, footnote c. [c] An acetonitrile solution of mesylate was injected. [d] Refer to Table 1, footnote g.

suitable for the solvolyses of mesylates, which are not as reactive as those we studied earlier.[2,11] The reactions of the *exo*-tosylate **11** in the presence of 1-butyl tosylate were also monitored by HPLC; as separate peaks were then obtained for the two tosylates, both rate constants were obtained (Tables 1 and 2).

The *exo*-tosylate **11** reacted three times as fast as 1-butyl tosylate (three measurements, Tables 1 and 2). Normally, β-branching reduces the rates of S_N2 reactions, for example, in ethanol at 50 °C, *iso*-butyl benzenesulfonate reacts 14-fold slower than 1-propylbenzenesulfonate.[12] These results provide some evidence of enhanced rates for the solvolyses of **11**. Relative rates of solvolyses of geometrically constrained cyclopropylcarbinyl systems depend strongly on the angle of rotation of the cyclopropane group against the planar cationic subunit.[13] Rates may be strongly enhanced, but in a constrained perpendicular conformation, rates may even be reduced by a factor of about 200.[13] Although rotation in **11** is not prevented, the preferred direction of attack by a nucleophile may lead to a transition state of nonoptimal conformation having a partial positive charge on the carbinyl carbon atom.

Reactions of **11** in methanol were faster in the presence of higher concentrations of methoxide base (Table 1, footnote i),

CHART 1



supporting an S_N2 mechanism (see also the above discussion of Scheme 6). Although low concentrations of the nucleophile triethylamine were present in the solutions used for the kinetic studies, very similar rate constants were obtained for methanolyses in the presence 0.003 and 0.01 M triethylamine (Table 1), so the data should refer to the pseudo-first-order rate constants for methanolysis. However, the rate constants for the corresponding S_N1 solvolyses via the cation *exo*-**18** would be lower.

Similar considerations apply to the experiments with acetone/water, with added triethylamine. As conditions for preparative studies (Scheme 6) involve about 100-fold higher concentrations of tosylate **11** and triethylamine than conditions for kinetic studies (Table 2), the formation of the salt **17** is less likely in the kinetic studies. The kinetic monitoring by HPLC with UV detection reveals only the formation of *p*-toluenesulfonic acid as product, but the effect of changes in the nucleophile concentrations can be illustrated using published data for methyl tosylate; in methanol at 25 °C, second-order rate constants for the reaction with triethylamine are over 20 000-fold greater than calculated values for methanolysis,[14] but 0.003 M triethylamine is 10 000-fold more diluted than the methanol solvent. As competing S_N2 reactions should show a rate/product correlation, methanolysis and aminolysis are competitive reactions in very dilute amine solutions, even for the less-hindered methyl tosylate. Consequently, methanolysis of **11** should proceed under kinetic conditions in addition to aminolysis. Another indication of the consistency of the data is the similarity of the rate constants for both methanolysis and hydrolysis (in 60% acetone/water) of **11**, comparing again with an S_N2 mechanism for methyl tosylate, the rate constants of which are 1.06×10^{-5} and 1.38×10^{-5} s^{-1} in methanol and 60% acetone/water, respectively, at 50 °C.[15]

In contrast, the rates of solvolyses of the *endo*-mesylate **10** increase 70-fold from methanol to 40% acetone/water, showing a significant dependence on the solvent ionizing power but less than that for the solvolyses of cyclopropylcarbinyl substrates.[16] Rates for **10** are similar to those of the solvolyses of the corresponding monocyclic compound, that is, cyclopropylcarbinyl mesylate (**19**, Chart 1). In 60% acetone/water at 25 °C, the rate constant for **19** is 5.25×10^{-3} s^{-1},[3] that is three times as large as that of **10** (Table 2). A cationic (S_N1) mechanism in which rearrangement accompanies ionization accounts for the kinetic data and also for the products (Scheme 5). As **11** and **10** react by different mechanisms, the exo/endo rate ratio is solvent dependent and varies from 1:300 in methanol at 40 °C (Table 1) to 1:3600 in 60% acetone/water at 25 °C (Table 2).

(10) Bentley, T. W.; Carter, G. E. *J. Org. Chem.* **1983**, *48*, 579−584.
(11) Bentley, T. W.; Kirmse, W.; Llewellyn, G.; Söllenböhmer, F. *J. Org. Chem.* **1990**, *55*, 1536−1540.
(12) Laughton, P. M.; Robertson, R. E. *Can. J. Chem.* **1955**, *33*, 1207−1215.
(13) Rhodes, Y. E.; DiFate, V. G. *J. Am. Chem. Soc.* **1972**, *94*, 7582−7583.
(14) Pearson, R. G.; Songstad, J. *J. Org. Chem.* **1967**, *32*, 2899−2900.
(15) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667−7674.
(16) Kevill, D. N.; Abduljaber, M. H. *J. Org. Chem.* **2000**, *65*, 2548−2554.

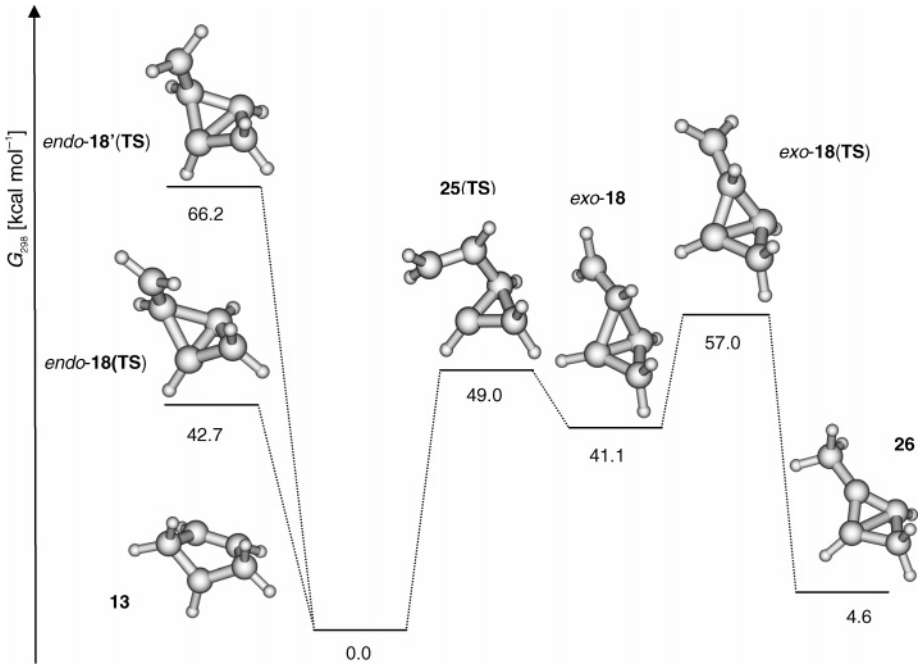


FIGURE 1. Structure and relative free energies computed for the C_5H_7 cations **13**, **18**, **25**, and **26**. The label **TS** characterizes a species as a transition state.

For the reasons discussed above, these ratios overestimate the S_N1 reactivity of **11**. Consequently, the **11**/**10** (*exo*/*endo*) rate ratio for S_N1 reactions must be even less than the above estimates, whereas the exo/endo rate ratio is 2 for the solvolyses of **2**.[1] The reasons for this major difference are explored theoretically in the next section.

The difference between the rate of **10** and the rate of **11** as well as the fact that both solvolyse more slowly than **19** calls for an explanation. A clue is provided by the reactivity of the bicyclo[1.1.0]but-1-ylcarbinyl esters **21** and **22** (Chart 1). The tosylate **21** could not be obtained as a result of its rapid rearrangement to 3-methylenecyclobutyl tosylate,[17] but the intermediacy of the bicyclo[1.1.0]but-1-ylcarbinyl cation (**24**, Chart 1) is highly likely because **24** was observed directly in a non-nucleophilic medium.[18] Estimated roughly, the rate of solvolysis of the *p*-nitrobenzoate **22** is 1000 times greater than that of cyclopropylcarbinyl *p*-nitrobenzoate (**20**).[17] This difference is caused by the availability for participation of the electrons of the C−C bonds adjacent to the cationic center. The more p character these bonds have, the more stabilized is the cation and, hence, the higher the rate of solvolysis.

Whereas the p character of these bonds amounts to 80% in the cyclopropylcarbinyl cation (**23**), it is much larger for the bond between the bridgehead carbon atoms of **24**, which is considered to be formed from electrons in the almost pure p orbitals.[19] A consequence of this high p character of the central bicyclo[1.1.0]butane bond is that the lateral bonds are formed from electrons in orbitals with less p character than those of the C−C bonds of cyclopropane. Being the participating ones in the bicyclo[1.1.0]but-2-ylcarbinyl cations (**18**, Scheme 6 and Figure 1), such lateral bonds emerge from the orbitals of C2 on one side and C1 and C3 on the other, having 80 and 70% p character, respectively.[19] Thus, the corresponding electrons are less suitable for participation than the respective ones of **23**, causing the slow solvolysis of the *exo*-tosylate **11**. The same effect should be operative in the case of the *endo*-mesylate **10**, but there the *endo*-bicyclo[1.1.0]but-2-ylcarbinyl cation is bypassed during solvolysis as a result of the concomitant Wagner−Meerwein rearrangement [see *endo*-**18(TS)** in Figure 1], which brings about a significant release of strain energy and, therefore, almost compensates the rate-retarding effect of the participating bonds in comparison with **19**. Such compensation is not possible for the *exo*-tosylate **11** because of the inability of the cation *exo*-**18** to undergo a conventional Wagner−Meerwein rearrangement (see next section).

The introduction of a second OMs or OTs group facilitated our earlier work by deactivating the substrates.[2,4] The magnitude of the effect in a relatively flexible substrate can be calculated from the solvolysis rates of the *endo*-mesylate **10** and *endo*,*endo*-**4**. In acetone/water at 25 °C, the ratio amounts to 21 and 31 (60%, 1.75×10^{-3} s^{-1} versus 8.2×10^{-5}; 40%, 1.00×10^{-2} versus 3.24×10^{-4}; data from Table 2 and ref 4) and is, thus, 20- to 30-fold less than we expected previously.[4]

3. Calculations of the Stability and the Rearrangements of the Bicyclo[1.1.0]butyl-2-carbinyl Cations. Computational Details. All structures were optimized by means of analytical gradients in combination with the B3LYP functional[20] in the TZVP (triple zeta valence quality with polarization functions)[21] basis set, which for carbon represents an (11s6p1d) atomic orbital (AO) basis in a [5s3p1d] contraction and for hydrogen a (10s1p) AO basis in a [4s1p] contraction. Solvent effects were estimated with the aid of COSMO (conductor-like screening model)[22] with a dielectric constant of $\epsilon = 30$ to simulate the acetone solvent. Energy minima and transition states were

(17) Wiberg, K. B.; Lampman, G. M.; Cuila, R. P.; Connor, D. S.; Schertler, P.; Lavanish, J. *Tetrahedron* **1965**, *21*, 2749−2769.
(18) Wiberg, K. B.; McMurdie, N. *J. Org. Chem.* **1993**, *58*, 5603−5604.
(19) Wiberg, K. B. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: Chichester, England, 1987; Part 1, pp 1−26.
(20) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
(21) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829−5835.

TABLE 3. Gas-Phase Energies (ΔE, $\epsilon = 1$), Gas-Phase Free Energies (ΔG, $\epsilon = 1$), and Energies in Solution (ΔE, $\epsilon = 30$) of Various C_5H_7 Cations, Relative to the Corresponding Values of 13[a]

cation	ΔE (B3LYP/TZVP; $\epsilon = 1$)	ΔG_{298} (B3LYP/TZVP; $\epsilon = 1$)	ΔE (B3LYP/TZVP; $\epsilon = 30$)
endo-**18(TS)**	40.7	42.7	41.2
endo-**18′(TS)**	65.3	66.2	64.7
exo-**18**	40.6	41.1	41.3
exo-**18(TS)**	59.5	57.0	
25(TS)	51.8	49.0	
26	4.1	4.6	3.6

[a] See Figure 1; in kcal mol^{-1}.

checked by frequency calculations. All computations were performed with the Turbomole program package,[23] which also allowed the determination of thermodynamic corrections by the standard implementation.

***endo*- [*endo*-18(TS)] and *exo*-Bicyclo[1.1.0]but-2-ylcarbinyl Cations (*exo*-18).** The gas-phase energies of the C_5H_7 cations **18**, **25**, and **26**, relative to the value of **13**, are collected in Table 3. In addition, the corresponding ΔG values at 298 K are contained as well as the energies in solution ($\epsilon = 30$) of species **18** and **26**, again relative to the corresponding data of **13**. Solvent effects are not discussed specifically because they do not seem to be of particular importance with regard to the energy differences, as calculations have shown for the cyclopropylcarbinyl cation and its isomers.[24] Also, thermodynamic corrections do not cause significant changes in this respect. Figure 1 displays the structures of **13**, **18**, **25**, and **26**, which are grouped according to their relative free energies and their fates on rearrangement.

Two conformations of the *endo*-bicyclo[1.1.0]but-2-yl cation have been calculated. As expected, in analogy to the most stable form of the cyclopropylcarbinyl cation,[24−26] the bisected structure [*endo*-**18(TS)**] is much lower in energy than the perpendicular one ([*endo*-**18′(TS)**]), with the free energy difference being 23.5 kcal mol^{-1}. Neither of these two cations is an energy minimum, as both undergo a [1,2]-C migration without an activation barrier to give the nonclassical cyclopent-3-en-1-yl cation (**13**). In fact, *endo*-**18(TS)** and *endo*-**18′(TS)** are transition states for automerization pathways of **13**, which have no significance, however, because the isomerization of **13** leading to the cyclopent-2-en-1-yl cation, brought about by a [1,2]-H shift, has a much lower activation barrier.[27] The nonclassical nature of **13**, being a bishomocyclopropenyl cation, has previously been demonstrated by calculations[28,29] that, hence, predicted a folded structure as the ground state and a planar five-membered ring (classical cyclopent-3-en-1-yl cation) as the transition state for the interconversion of the degenerate envelope forms. The latter was calculated to be more stable by 4.5 kcal mol^{-1} than the planar isomer after the correction for the zero-point energy.[29]

The finding that *endo*-**18(TS)** and *endo*-**18′(TS)** reorganize to furnish **13** without an activation barrier corroborates our previous assumption of the Wagner−Meerwein rearrangement as proceeding simultaneously with the dissociation during most solvolyses of corresponding bicyclo[1.1.0]but-2-ylcarbinyl substrates. Thus, derivatives of *endo*-**18(TS)**, which might be thought to be generated from *endo*,*endo*-**4**, tricyclo[3.1.0.0^{2,6}]-hex-3-yl sulfonates, and tricyclo[4.1.0.0^{2,7}]hept-3-yl esters, cannot be considered as intermediates.[2−4] Only in the case of tricyclo[4.1.0.0^{2,7}]hept-4-en-3-yl *p*-nitrobenzoate, which was the sole substrate to furnish nonrearranged solvolysis products to some extent, the intermediacy of the tricyclo[4.1.0.0^{2,7}]hept-4-en-3-yl cation, which is an allyl cation bridged by a bicyclo-[1.1.0]butane system, seems possible at least.[3]

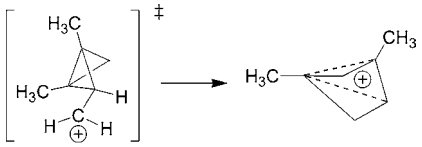
In contrast to *endo*-**18(TS)**, the *exo*-bicyclo[1.1.0]but-2-ylcarbinyl cation in the bisected conformation (*exo*-**18**) indeed represents an energy-minimum structure, as expected for a cyclopropylcarbinyl cation;[25] its free energy (41.1 kcal mol^{-1}, Table 3, Figure 1) is very similar to that of *endo*-**18(TS)**. The calculations show that the most favorable isomerization of *exo*-**18** leads also to **13**. However, the mechanism of the process is not a simple Wagner−Meerwein rearrangement, but one that occurs in two stages. Its transition state has a structure resembling that of the 2-vinylcycloprop-1-yl cation [**25(TS)**], whose free energy is 7.9 kcal mol^{-1} greater than that of *exo*-**18**. In line with this result, we have pointed out previously that the inability of the cation conceivably generated from *exo*,*exo*-**4** (Scheme 2) to undergo a [1,2]-C shift might be the reason for the exclusive formation of unrearranged products such as **6**, even if S_N2 reactions of *exo*,*exo*-**4** could not be rigorously ruled out.[4] The substitution products, **16** and **17**, from the solvolyses of **11** support this interpretation.

There is a second, less favorable, pathway for *exo*-**18** to release most of its considerable strain energy, namely, a [1,2]-H migration to the cationic center giving rise to **26**, which also is a homoaromatic species, that is, the nonclassical 2-methylcyclobutenyl cation. The transition state [*exo*-**18(TS)**] is the slightly twisted perpendicular conformation of the *exo*-bicyclo-[1.1.0]but-2-ylcarbinyl cation. By an extensive study using theoretical methods, the homoaromatic nature of the unsubstituted cyclobutenyl cation, the parent of **26**, has been demonstrated.[30]

Introduction of Methyl Groups into the Bridgehead Positions of the Bicyclo[1.1.0]but-2-ylcarbinyl Cations. The replacement of the hydrogen atoms of the positions 1 and 3 of all species **18** by methyl groups has a dramatic effect on the shape of the potential energy surface. While *exo*-**18** represents a local minimum and has to surmount a barrier of 7.9 kcal mol^{-1} to rearrange to **13**, its methylated counterpart **27(TS)** converts into **28** (Scheme 7), which is the 1,3-dimethyl derivative of **13**, without any barrier. Because the positive charge of **25(TS)** largely resides at a carbon atom whose hydrogen atom is

(22) Klamt, A.; Schüürmann, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799−805.
(23) Ahlrichs, R.; Bär, M.; Baron, H.-P.; Bauernschmitt, R.; Böcker, S.; Deglmann, P.; Ehrig, M.; Eichkorn, K.; Elliott, S.; Furche, F.; Haase, F.; Häser, M.; Horn, H.; Hättig, C.; Huber, C.; Huniar, U.; Kattannek, M.; Köhn, A.; Kölmel, C.; Kollwitz, M.; May, K.; Ochsenfeld, C.; Öhm, H.; Schäfer, A.; Schneider, U.; Sierka, M.; Treutler, O.; Unterreiner, B.; von Arnim, M.; Weigend, F.; Weis, P.; Weiss, H. *TURBOMOLE*, version 5.6; Universität Karlsruhe: Germany, since 1988.
(24) Casanova, J.; Kent, D. R., IV; Goddard, W. A., III; Roberts, J. D. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 15−19.
(25) Saunders, M.; Laidig, K. E.; Wiberg, K. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7652−7659.
(26) Wiberg, K. B.; Shobe, D.; Nelson, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 10645−10652.
(27) Olah, G. A.; Prakash, G. K. S.; Rawdah, T. N.; Whittaker, D.; Rees, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 3935−3939.
(28) Schleyer, P. v. R.; Bentley, T. W.; Koch, W.; Kos, A. J.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 6953−6957.
(29) Szabo, K. J.; Kraka, E.; Cremer, D. *J. Org. Chem.* **1996**, *61*, 2783−2800.
(30) Sieber, S.; Schleyer, P. v. R.; Otto, A. H.; Gauss, J.; Reichel, F.; Cremer, D. *J. Phys. Org. Chem.* **1993**, *6*, 445−464.

SCHEME 7. Schematic Representation of the Relationship between the $C_5H_5(CH_3)_2$ Cations 27(TS) and 28



27(TS) $\Delta\Delta G_{298} = -42.5$ kcal mol^{-1} **28**

replaced by a methyl group, a substantial stabilization occurs. Such an effect is operative neither on going from *exo*-**18** to **27(TS)** nor on going from **13** to **28**, but both of these transitions are influenced in very much the same way, as is indicated by the energy differences between *exo*-**18** and **13** on one hand and between **27(TS)** and **28** on the other, which were calculated to be 41.1 (Figure 1, Table 3) and 42.5 kcal mol^{-1} (Scheme 7), respectively. Additionally, it can be assumed that the 1,3-dimethyl derivative of *endo*-**18(TS)** is also a transition state and retains an energy relative to that of **28** that is similar to the energy difference between *endo*-**18(TS)** and **13**.

Clearly, this result explains that the tosylates *endo*- and *exo*-**2** can furnish the common product **3**,[1] which emerges from the trapping of the cation **28** by water, and that both substrates may react at about the same rate. However, the 1,3-dimethylbicyclo-[1.1.0]but-2-ylcarbinyl cations [see **27(TS)**] cannot be considered as intermediates because the rearrangements should occur concomitant with the heterolytic dissociation.

Conclusion

Motivated by previous results that apparently contradicted each other,[1,4] we undertook to approach the problem by experimental and theoretical studies of the unsubstituted diastereomeric bicyclo[1.1.0]but-2-ylcarbinyl cations. The experiments included the development of a synthetic route to the two bicyclo[1.1.0]butane-2-methanols (**9**), their conversion into the mesylate **10** and the tosylate **11** in the case of the *endo*- and *exo*-isomer, respectively, and the determination of the products and the rates of the solvolysis reactions of **10** and **11**. Both mesylate **10** and tosylate **11** underwent solvolysis at smaller rates than cyclopropylcarbinyl mesylate (**19**), whereas bicyclo-[1.1.0]but-1-ylcarbinyl esters had previously been shown to react faster than the corresponding cyclopropylcarbinyl esters.[17] These phenomena are readily explained on the basis of the p character of the C−C bonds that can exert neighboring group participation on heterolytic dissociation.

The quantum chemical calculations revealed that the *endo*-bicyclo[1.1.0]but-2-ylcarbinyl cation is only a transition state [*endo*-**18(TS)**] for an automerization of the nonclassical cyclopent-3-en-1-yl cation (**13**), whereas the exo isomer corresponds to a local energy minimum (*exo*-**18**). In line with these predictions, the solvolyses of the *endo*-mesylate **10** gave rise to 4-substituted cyclopentenes exclusively, thus demonstrating that the Wagner−Meerwein rearrangement occurred concomitant with the heterolytic dissociation. The outcome of the solvolyses of the *exo*-tosylate **11** is formally also in agreement with the computational result, as only products with complete retention of the carbon atom skeleton were observed. However, the rate studies do not support the intermediacy of the cation *exo*-**18** but favor an S_N2 process.

Most interestingly, the introduction of methyl groups in positions 1 and 3 of *exo*-**18** is predicted to have a dramatic effect on the transition state that separates *exo*-**18** from **13**. It becomes more stable than the *exo*-1,3-dimethylbicyclo[1.1.0]but-2-ylcarbinyl cation, whereby this cation adopts the character of a transition state [**27(TS)**]. This finding explains the products and the rates of the solvolysis of the diastereomeric 1,3-dimethylbicyclo[1.1.0]but-2-ylcarbinyl tosylates (**2**)[1] in comparison with the results obtained from the diastereomeric pair *endo*,*endo*-(*endo*,*endo*-**4**) and *exo*,*exo*-bicyclo[1.1.0]but-2,4-dimethanol dimesylate (*exo*,*exo*-**4**)[4] as well as **10** and **11**.

Experimental Section

General Methods. See ref 4.

***erythro*- (*erythro*-8) and *threo*-2′,2′-Dibromocycloprop-1′-yloxirane (*threo*-8).** A solution of dimethyldioxirane[8] (2.50 mmol, 31.25 mL of 0.08 M in acetone) was added with stirring to 1,1-dibromo-2-vinylcyclopropane[7] (500 mg, 2.21 mmol), which was kept at 0 °C under nitrogen, within 50 min. Stirring was continued for 2 h at 0 °C and then overnight at room temperature. The mixture was concentrated in vacuo to give a light yellow oil (400 mg, 75%), which was shown by NMR spectroscopy to consist of a virtually pure 1:1 mixture of *erythro*- and *threo*-**8**. Flash chromatography [SiO_2; light petroleum ether (bp 30−50 °C)/*tert*-butyl methyl ether, 20:1] afforded pure *threo*-**8** (150 mg, 28%) and pure *erythro*-**8** (170 mg, 32%). *threo*-**8**: $R_f = 0.47$, colorless crystals, mp 41−43 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63 (t, $J = 7.3$ Hz, 1H), 1.76 (dd, $J = 10.3$, 7.2 Hz, 1H), 1.85 (ddd, $J = 10.3$, 7.4, 3.8 Hz, 1H), 2.64 (dd, $J = 5.1$, 2.6 Hz, 1H), 2.89 (dd, $J = 5.1$, 3.9 Hz, 1H), 3.09 (td, $J = 3.8$, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 23.4 (s), 24.8 (t), 31.8 (d), 45.9 (t), 50.7 (d). Anal. Calcd for $C_5H_6Br_2O$: C, 24.83; H, 2.50. Found: C, 25.06; H, 2.44. *erythro*-**8**: $R_f = 0.34$, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.54 (t, $J = 7.4$ Hz, 1H), 1.61 (br dt, $J = 10.1$, 7.2 Hz, 1H), 1.84 (dd, $J = 10.1$, 7.2 Hz, 1H), 2.70 (dd, $J = 4.9$, 2.6 Hz, 1H), 2.87 (br t, $J = 4.4$ Hz, 1H), 2.95 (br ddd, $J = 7.0$, 3.7, 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 23.8 (s), 26.0 (t), 32.0 (d), 46.1 (t), 53.2 (d). Anal. Calcd for $C_5H_6Br_2O$: C, 24.83; H, 2.50. Found: C, 24.97; H, 2.53.

***endo*-Bicyclo[1.1.0]butane-2-methanol (*endo*-9).** *n*-Butyllithium (5.00 mmol, 3.31 mL of 1.51 M in hexane) was added dropwise within 35 min to a stirred solution of *threo*-**8** (550 mg, 2.27 mmol) in anhydrous diethyl ether (40 mL), which was kept at −75 °C under nitrogen. Stirring was continued for 1.5 h at −75 to −70 °C and then for 1 h at 20 °C. The mixture was treated with water (5 mL), the resulting layers were separated, the aqueous phase was extracted with diethyl ether (3 × 10 mL), and the combined organic phases were washed with brine (2 × 25 mL). After drying with Na_2SO_4, the solution was concentrated in vacuo (500−250 mbar) at 20 °C. A ^{1}H NMR spectrum of the residue indicated the presence of *endo*-**9**, 1-bromobutane, and 1-butanol. The desired product, *endo*-**9**, was enriched by a slow evaporation of the volatile components of the mixture in vacuo (250−0.07 mbar) at 20 °C and their condensation in cooled receivers. The first fractions consisted mainly of 1-bromobutane and 1-butanol, whereas the last fractions contained *endo*-**9** as the major component. Out of a number of experiments, the best fraction obtained was a colorless liquid (66 mg) composed of *endo*-**9** (32% yield) and 1-butanol in the ratio of about 15:1 and only traces of other impurities. ^{1}H NMR (400 MHz; C_6D_6; the chemical shifts in $CDCl_3$ are given in brackets): δ 0.89 [1.15] (t, $J = 5.9$ Hz, 1H), 1.14 [1.52] (td, $J = 3.3$, 1.7 Hz, 2H), 1.25 [1.44] (qq, $J = 1.7$, 0.5 Hz, 1H), 1.48 [1.84] (qd, $J = 3.3$, 1.7 Hz, 1H), 2.38 [2.68] (tqd, $J = 7.2$, 3.3, 0.6 Hz, 1H), 3.21 [3.36] (br dd, $J = 7.2$, 5.9 Hz, 2H). ^{13}C NMR (101 MHz; C_6D_6; the chemical shifts in $CDCl_3$ are given in brackets): δ 1.7 [1.4] (dsext, $J_{C,H} = 201.3$, 3.5 Hz, 2C), 30.3 [30.2] (dddt, $J_{C,H} = 170.6$, 151.4, 12.7, 4.2 Hz, 1C), 49.7 [49.4] (ddquint, $J_{C,H} = 150.7$, 14.2, 3.4 Hz, 1C), 56.0 [56.3] (br t, $J_{C,H} = 141.5$ Hz, 1C). MS (EI, 70 eV, %) *m*/*z*: M^+ 84 (11), 83 (35), 69 (14), 67 (10), 56 (33), 55 (100), 54 (11), 53 (24), 43 (15), 41 (44), 39 (35); the intensity of

several signals may have a contribution from 1-butanol. HRMS (EI, 70 eV) *m*/*z*: [$M^+ - H$] calcd for C_5H_7O, 83.0497; found, 83.0495.

***exo*-Bicyclo[1.1.0]butane-2-methanol (*exo*-9).** According to the procedure for the preparation of *endo*-**9**, *exo*-**9** (28%) was obtained from *erythro*-**8** (1.25 g, 5.17 mmol) in the best case as a 4:1 mixture (150 mg, colorless liquid) with 1-butanol, containing only traces of other impurities. ^{1}H NMR (400 MHz; $CDCl_3$; the chemical shifts in C_6D_6 are given in brackets): δ 0.60 [0.53] (qd, J = 1.2, 0.9 Hz, 1H), 1.16 [1.05] (tdtd, J = 5.8, 1.2, 0.9, 0.4 Hz, 1H), 1.28 [0.95] (br, 1H), 1.45 [1.18] (ddd, J = 2.9, 1.2, 0.9 Hz, 2H), 1.50 [1.27] (tdd, J = 2.9, 0.9, 0.4 Hz, 1H), 3.55 [3.25] (t, J = 5.8 Hz, 2H). ^{13}C NMR (101 MHz; C_6D_6; the chemical shifts in $CDCl_3$ are given in brackets): δ −0.3 [−0.7] (dquint, $J_{C,H}$ = 203.7, 3.8 Hz, 2C), 28.2 [28.1] (ddq, $J_{C,H}$ = 169.1, 153.0, 4.2 Hz, 1C), 46.0 [45.5] (ddm, $J_{C,H} \approx$ 170, 13 Hz, 1C), 62.1 [62.5] (tm, $J_{C,H} \approx$ 141 Hz, 1C). MS (EI, 70 eV, %) *m*/*z*: M^+ 84 (3), 83 (9), 56 (100), 55 (39), 44 (18), 43 (48), 42 (27), 41 (66), 40 (57), 39 (17); the intensity of several signals may have a contribution from 1-butanol. HRMS (EI, 70 eV) *m*/*z*: [$M^+ - H$] calcd for C_5H_7O, 83.0497; found, 83.0496.

***endo*-Bicyclo[1.1.0]but-2-ylcarbinyl Mesylate (10).** A stirred solution of *endo*-**9** (14 mg, 0.17 mmol), containing some 1-butanol, and dry triethylamine (25 mg, 0.25 mmol) in anhydrous dichloromethane (0.5 mL) was kept at −36 °C under nitrogen and treated dropwise with methanesulfonyl chloride (19 mg, 0.17 mmol) in anhydrous dichloromethane (0.2 mL) within 8 min. Stirring was continued for 90 min at −35 to −30 °C, while the progress of the reaction was monitored by TLC on basic Al_2O_3 (activity I) with petroleum ether (bp 30−50 °C)/*tert*-butyl methyl ether, 5:4. The mixture was then allowed to warm to −5 °C and, after the addition of 2 mL of cold dichloromethane, was washed quickly with ice-cold water (2 × 3 mL). The organic phase was dried with K_2CO_3/Na_2SO_4 and then concentrated in vacuo at 0−5 °C. The NMR spectra of the residue (20 mg of a light yellow oil) were taken at 27 °C and showed the presence of the mesylate **10**, 1-butyl mesylate, dichloromethane, and water. The sample was kept at −30 °C until further use. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.44 (m, 1H), 1.71 (td, J = 3.2, 1.4 Hz, 2H), 1.88 (qd, J = 3.2, 2.2 Hz, 1H), 2.73 (tqd, J = 7.3, 3.3, 0.5 Hz, 1H), 3.03 (s, 3H), 4.05 (d, J = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 2.0 (dsext, $J_{C,H}$ = 205.8, 3.5 Hz, 2C), 29.8 (dddt, $J_{C,H}$ = 170.5, 153.5, 12.2, 4.3 Hz, 1C), 37.9 (q, $J_{C,H}$ = 139.0, 1C), 44.8 (dm, $J_{C,H} \approx$ 156 Hz, 1C), 65.1 (t, $J_{C,H}$ = 150.5, 1C).

In a preceding experiment, $CDCl_3$ was used as the solvent and the NMR spectra were taken at −30 °C without workup, which clearly indicated the presence of **10**. As compared to the data of the salt-free solution obtained at 27 °C, the lower temperature and the presence of $HNEt_3^+Cl^-$ caused upfield shifts of about 0.3 ppm in the ^{1}H NMR spectrum and of up to 1.0 ppm in the ^{13}C NMR spectrum. After the sample had been kept at room temperature for a day, the spectra showed that 40% of the amount of **10** had been converted into cyclopent-3-en-1-yl mesylate (**12**) and a second 4-substituted cyclopentene, which could not be identified due to the signals of the impurities, whereas **12** was characterized by comparison of its signals with those of an authentic sample. The consumption of **10** was complete after 9 days at room temperature.

***exo*-Bicyclo[1.1.0]but-2-ylcarbinyl Tosylate (11)**. Sodium hydride (50 mg, 2.1 mmol) was added cautiously in several portions to a stirred solution of *exo*-**9** (57 mg, 0.68 mmol), containing 20% of 1-butanol, in anhydrous THF (3 mL), which was kept at 0−5 °C under nitrogen, within 30 min. Sodium hydride had been purchased as a suspension in paraffin oil and washed carefully with petroleum ether (bp 30−50 °C) before use. The mixture was stirred overnight at room temperature, then cooled to −17 °C, and treated dropwise with a solution of *p*-toluenesulfonyl chloride (190 mg, 1.0 mmol) in anhydrous THF (1 mL). Stirring was continued for 2 h at −15 °C. Then water (3 mL) was added, and the mixture was extracted with diethyl ether (2 × 10 mL). The combined organic phases were washed with 5% aqueous $NaHCO_3$ (2 × 10 mL) and finally with water (2 × 5 mL). Drying of the organic layer with K_2CO_3/Na_2SO_4 and its concentration in vacuo furnished a colorless oil (115 mg), shown by NMR spectroscopy to be a 4:1 mixture of **11** (57%) and 1-butyl tosylate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.56 (br quint, J = 1.0 Hz, 1H), 1.09 (tm, J = 6.3 Hz, 1H), 1.44 (td, J = 2.9, 0.8 Hz, 1H), 1.54 (ddd, J = 2.9, 0.9, 0.5 Hz, 2H), 2.45 (s, 3H), 3.93 (d, J = 6.3 Hz, 2H), 7.34 (m, 2H), 7.79 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 0.5 (dquint, $J_{C,H}$ = 207.4, 3.9 Hz, 2C), 21.6 (qt, $J_{C,H}$ = 127.3, 4.3 Hz, 1C), 27.7 (ddm, $J_{C,H}$ = 170, 154 Hz, 1C), 40.0 (dm, $J_{C,H} \approx$ 170 Hz, 1C), 69.7 (tm, $J_{C,H} \approx$ 150 Hz, 1C), 127.9 (dm, $J_{C,H} \approx$ 165 Hz, 2C), 129.8 (dm, $J_{C,H} \approx$ 162 Hz, 2C), 133.2 (m, 1C), 144.7 (m, 1C).

Solvolysis of 10 in 75% Aqueous Acetone. Triethylamine (50 mg, 0.49 mmol) and the mesylate **10** (20 mg, 0.12 mmol), containing some 1-butyl mesylate, were dissolved in a minimum quantity of acetone (1.5 mL). After the addition of water (0.5 mL), the mixture was stirred at 22 °C for 18 h. Then most of the acetone was evaporated in vacuo. Brine was added to the residue, and the mixture was extracted with *tert*-butyl methyl ether (4 × 5 mL). The combined extracts were dried with $MgSO_4$ and concentrated in vacuo to give a colorless oil, which was shown by NMR spectroscopy to contain cyclopent-3-en-1-yl mesylate (**12**) and cyclopent-3-en-1-ol (**14**) in the ratio of 2:1, 1-butyl mesylate, and a number of impurities but no product with a bicyclo[1.1.0]but-2-ylcarbinyl group. The signals of **12** and **14** were identified by comparison with those of authentic samples.

Solvolysis of 10 in [D_4]Methanol/Sodium [D_3]Methoxide. A solution of $NaOCD_3$ in $DOCD_3$ [9 mg of sodium (0.4 mmol) had been dissolved in $DOCD_3$ (0.7 mL)] was added to the mesylate **10** (20 mg, 0.12 mmol), containing some 1-butyl mesylate, in an NMR tube at 22 °C. After several minutes, a ^{1}H NMR spectrum showed the presence of **10**, cyclopent-3-en-1-yl mesylate (**12**), and [D_3]-methyl cyclopent-3-en-1-yl ether (**15**) in the ratio of 20:1:2.4. This ratio changed to 1.3:1:3.6 within 2.5 h, and **10** was consumed completely after 8.5 h with the **12**:**15** ratio being 1:6.5. Simultaneously, 1-butyl mesylate was consumed to the extent of about 40% and converted into 1-butyl [D_3]methyl ether within 8.5 h. ^{1}H NMR of **15** (400 MHz; $DOCD_3$; internal reference, $DOCHD_2$ at δ = 3.31): δ 2.33 (apparent ddm, line distances 16, 3 Hz, 2H), 2.56 (apparent ddm, line distances 16, 7 Hz, 2H), 4.12 (tt, J = 7.0, 3.2 Hz, 1H), 5.66 (m, 2H). ^{13}C NMR of **15** (101 MHz; $DOCD_3$; internal reference, $DOCD_3$ at δ = 49.0): δ 41.1, 59.7 (m, $J_{C,D}$ = 22 Hz), 82.1, 129.2.

Solvolysis of 11 in [D_4]Methanol/Sodium [D_3]Methoxide. A stock solution of $NaOCD_3$ in $DOCD_3$ was prepared by dissolution of sodium (42 mg, 1.83 mmol) in $DOCD_3$ (3 mL). When a mixture of **11** and 1-butyl tosylate was added to 0.7 mL of this solution or one that had been diluted 1:1 with pure $DOCD_3$, the substrates were transformed to *exo*-bicyclo[1.1.0]but-2-ylcarbinyl [D_3]methyl ether (**16**) and 1-butyl [D_3]methyl ether, respectively, within several days at 22 °C. The progress of the reactions was monitored by NMR spectroscopy. For the quantitative analysis, the integral of the signals of all aromatic protons of the sample was taken as the internal standard. The ratio of **11** and 1-butyl tosylate remained constant throughout the reactions, and the conversion of 1-butyl tosylate to 1-butyl [D_3]methyl ether was virtually quantitative.

On reaction of 13.5 mg (0.057 mmol) of **11** and 6.5 mg (0.028 mmol) of 1-butyl tosylate in 0.7 mL of the above stock solution (0.43 mmol of $NaOCD_3$ in $DOCD_3$), **11** was consumed to the extent of 37, 61, 83, 88, and 89% within 6, 9, 21.5, 26, and 30 h, respectively, and the yield of **16** amounted to 30, 48, 67, 69, and 74% after the same time periods.

On reaction of 6 mg (0.025 mmol) of **11** and 3 mg (0.013 mmol) of 1-butyl tosylate in a mixture of 0.35 mL of the above stock solution (0.22 mmol of $NaOCD_3$ in $DOCD_3$) and 0.35 mL of pure $DOCD_3$, **11** was consumed to the extent of 22, 66, 87, and 91% within 4, 24, 48, and 62.5 h, respectively, and the yield of **16** amounted to 16, 47, 67, and 82% after the same time periods.

^{1}H NMR of **16** (400 MHz; $DOCD_3$; internal reference, $DOCHD_2$ at $\delta = 3.31$): δ 0.51 (m, 1H), 1.02 (br t, $J = 6.1$ Hz, 1H), 1.46−1.49 (m, 3H), 3.31 (d, $J = 6.1$ Hz, 2H). ^{13}C NMR of **16** (101 MHz; $DOCD_3$; internal reference, $DOCD_3$ at $\delta = 49.0$): δ 0.1, 28.5, 43.4, 73.1; the septuplet of the CD_3 group was not observed due to its low intensity.

Solvolysis of 11 in a Mixture of 90% [D$_6$]Acetone/Water and Triethylamine. In an NMR tube, 20 mg of a 4:1 mixture of **11** (0.068 mmol) and 1-butyl tosylate (0.017 mmol) and triethylamine (17 mg, 0.17 mmol) were dissolved in 90% (v/v) $(CD_3)_2CO/H_2O$ (0.7 mL). A ^{1}H NMR spectrum was taken right away. The sample was then kept at room temperature, and NMR spectra of it were taken over a period of 118 days. For the quantitative analysis, the integral of the signals of all aromatic protons of the sample was used as the internal standard. The products were (*exo*-bicyclo[1.1.0]-but-2-ylcarbinyl)triethylammonium tosylate (**17**) from **11** and 1-butyltriethylammonium tosylate from 1-butyl tosylate. Within 2, 7, 14, 32, 56, and 118 days, **11** was consumed to the extent of 3, 11, 19, 34, 49, and 71%, respectively, whereas the yield of **17** was determined to be 2, 5, 11, 22, 34, and 41% after the same time periods. The ratio of unreacted **11** and 1-butyl tosylate remained constant over 118 days, and the yield of 1-butyltriethylammonium tosylate was about 80%.

^{1}H NMR of **17** [400 MHz; $(CD_3)_2CO/H_2O$, 9:1; internal reference, CHD_2COCD_3 at $\delta = 2.09$]: δ 0.59 (br quint, $J = 1.1$ Hz, 1H), 1.08 (br t, $J = 6.3$ Hz, 1H), 1.37 (tt, $J_{H,H} = 7.2$, $J_{H,N} = 1.7$ Hz, 9H), 1.53 (td, $J = 2.9$, 0.7 Hz, 1H), 1.88 (dt, $J = 2.9$, 0.8 Hz, 2H), 2.34 (s, 3H), 3.39 (d, $J = 6.3$ Hz, 2H), 3.48 (q, $J = 7.2$ Hz, 6H), 7.18 (m, 2H), 7.71 (m, 2H). ^{13}C NMR of **17** [101 MHz; $(CD_3)_2CO/H_2O$, 9:1; internal reference, $(CD_3)_2CO$ at $\delta = 29.9$]: δ 1.2, 7.8, 21.2, 28.3, 35.0, 53.9 (t, $^1J_{C,N} = 2.7$ Hz), 57.6 (t, $^1J_{C,N} = 3.3$ Hz), 126.8, 129.1, 139.8, 144.9.

Kinetic Methods. Standard procedures, as described elsewhere,[4] were used for conductometric measurements, but the following slightly revised method was used for mesylates. To the alcohol *endo*-**9** (1.7 mg), in a Wheaton bottle fitted with a magnetic stirrer and sealed with a septum (having a pressure release needle), was added a solution of 2.5 equivalents (7 μL) of triethylamine (stored over KOH) in dichloromethane (80 μL, AR grade). The solution was cooled to −10 °C, and methanesulfonyl chloride (1.4 μL, <1 equiv) in dichloromethane (20 μL) was added in portions slowly with stirring over 5−10 min. After stirring for another 5−10 min at −10 °C, an aliquot of the solution was injected directly into AR grade methanol (previously degassed by sonication) and further sonicated to disrupt any aggregates of dichloromethane. The solution was then transferred to a conductivity cell and thermostated, and the change in conductance was monitored.

HPLC measurements were obtained from a solution of *exo*-tosylate (**11**, 1−2 mg) in acetonitrile (40 μL) that was added to the solvolysis medium (10 mL); 10 × 1 mL aliquots were then sealed in glass ampules.[31] Aliquots (20 μL) of quenched reaction mixtures were analyzed using a Waters Novapak C_{18} column (15 cm) eluted with 65% (v/v) methanol/water, with detection at 225 nm ($A = 0.2$). Rate constants were calculated from the peak areas of the esters, and the "theoretical infinity" of the zero ester area was assumed.

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Supporting Information Available: Absolute energies and Cartesian coordinates of the structures of the cations **13**, **18**, and **25**−**28** as well as the ^{13}C NMR spectra of the new compounds and the solvolysis products. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) Bentley, T. W.; Gream, G. E. *J. Org. Chem.* **1985**, *50*, 1776−1778.