Effects of Bridgehead Substitution on Structure and Reactivity of the 7-Norbornyl Cation

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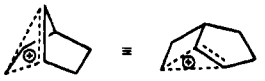
A systematic investigation was undertaken of the effect of bridgehead substitution on the solvolytic reactivity of 7-norbornyl triflates in aqueous TFE. Methyl substitution increases the rate 60-fold and the effect of multiple substitution is additive. Chlorine, on the other hand, exhibits a combined inductive and resonance effect and decreases the reactivity 1700 times. The observed normal secondary β-deuterium isotope effect of the 1,4-d_2 derivative can be rationalized by assuming a tilted C_s geometry for the cationic transition structure which is only slightly higher in energy than the nonclassical intermediate cation of C_1 symmetry. Bridgehead methyl-d_3 kinetic isotope effects are similar to those associated with the nonmigrating methyl group in neopentyl ester solvolyses. These results are in agreement with the recently published structure of the 7-norbornyl cation calculated at the highest *ab initio* level which has confirmed its nonclassical nature as originally proposed by Winstein.

Introduction

A unique position as one of the least reactive secondary esters is held by 7-norbornyl tosylate. Its half-life in acetic acid when extrapolated to 25 °C is 3 450 000 years which makes it about 10^{10} times less reactive than the anchimerically assisted 2-norbornyl isomer. In spite of the absence of anchimeric acceleration, but because the unrearranged substitution products had retained configuration and the small degree of rearrangement afforded bicyclo[3.2.0]heptyl products, Winstein[1] proposed for the cationic intermediate the σ-delocalized structure **1** of C_1 symmetry.



1 (C_1)

Angle strain at C7 cannot be an important factor for the unreactivity of 7-norbornyl derivatives. Cyclobutyl and cyclopentyl β-naphthalenesulfonates where the angles in the corresponding hydrocarbons are 88.5° and 104.4°, respectively, show the same acetolysis rates which are 30 times *faster* than for the cylohexyl derivative (111.4°).[2] Steric hindrance to solvation due to *exo* hydrogens in 7-norbornyl derivatives is also an unlikely factor, because an analogous situation is found in 2-adamantyl sulfonate esters, which, however, react about 10^5 times faster. An acceptable explanation was given by Heilbronner and Hoffmann[3] who pointed out that for symmetry reasons the cationic center at C7 cannot gain any stabilization from the ribbon orbitals of the σ-skeleton of the underlying six-membered ring (Figure 1).

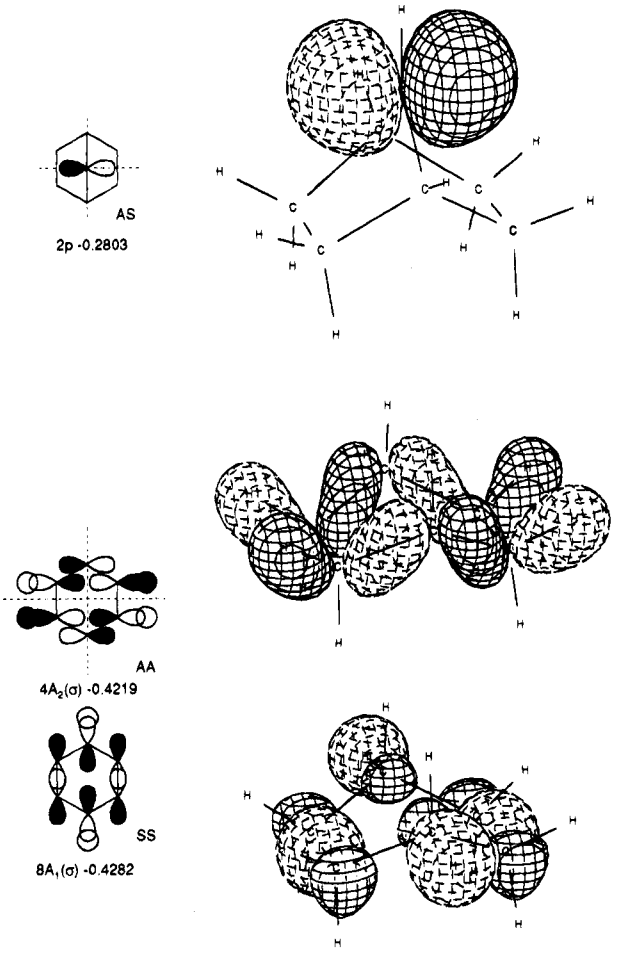


Figure 1. The symmetry-enforced absence of interaction between the highest-lying molecular orbitals of the boat cyclohexane substructure and the vacant 2p orbital in the 7 position of **2** (C_{2v}). Energies are given in hartrees calculated at the RHF/6-31G* level of theory.

Strictly, this refers only to the symmetric, C_{2v} structure **2** which, while found by low level (STO-3G) *ab initio*

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(1) Winstein, S.; Gadient, F.; Stafford, E. T.; Klinedinst, P. E. *J. Am. Chem. Soc.* **1958**, *80*, 5895.

(2) Brown, H. C. (with comments by Schleyer, P. v. R.) *The Nonclassical Ion Problem*; Plenum Press: New York and London, 1977; p 71.

(3) Hoffmann, R.; Mollere, P. D.; Heilbronner, E. *J. Am. Chem. Soc.* **1973**, *95*, 4860, and references therein.

0022-3263/94/1959-7051$04.50/0

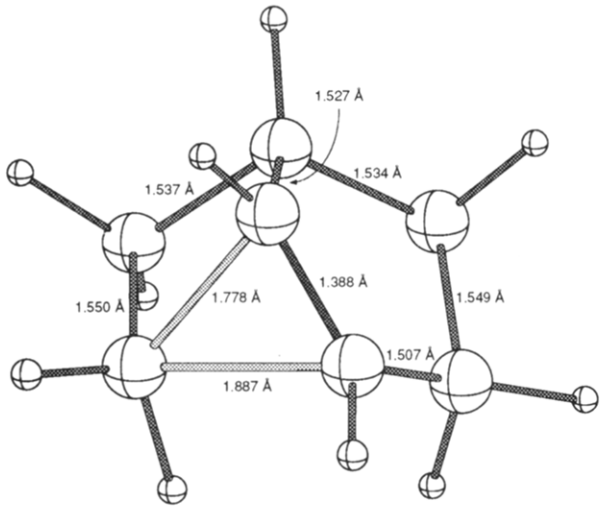
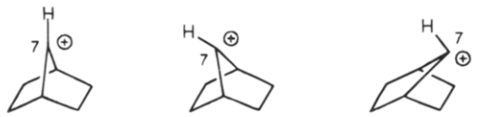


Figure 2. MP2(full)/6-31G* optimized structure of the 7-norbonyl cation.[7]

calculations to be a minimum on the potential energy surface, cannot explain the stereochemistry of the solvolysis products. Semiempirical calculations gave preference to the tilted structures **3** and **4** to which the same symmetry arguments can be applied.[4]



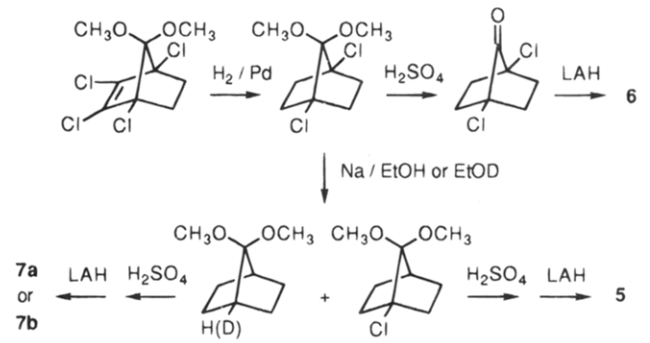
2 (C_{2v}) **3** (C_s) **4** (C_s)

Kirmse and collaborators[5] have extensively investigated substituent effects on the product composition in solvolysis and deamination reactions of 7-norbornyl and bicyclo[3.2.0]heptyl derivatives. Kinetic and product studies on the parent system have been reported by a number of authors,[6] but no definite conclusion could be reached regarding the structure of the solvolysis transition state and/or reactive intermediate.

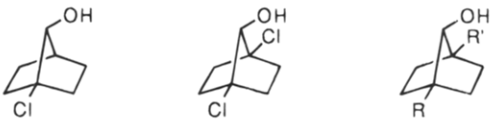
Recently by a combination of high level *ab initio* calculations and spectroscopic studies, the problem of the structure of the 7-norbornyl cation has been solved.[7] The C_1 structure **1** first proposed by Winstein[1] was shown to be a minimum on the potential energy surface at the MP4(sdq,fc)/6-31G**//MP2(full)/6-31G* level of theory (Figure 2). This was confirmed experimentally by isolation of this cation under stable-ion conditions in the SbF_5 matrix at 110 K and comparing the recorded IR spectrum with the calculated frequencies.[7a]

In this paper we report a kinetic study of the effect of bridgehead substitution on the solvolytic reactivity of

Scheme 1



7-norbornyl triflates in aqueous TFE. For this purpose compounds **5**–**9** as well as the deuterated derivatives **7b**–**9b** were prepared and the solvolysis rates of the corresponding triflates were determined in aqueous 2,2,2–trifluoroethanol (TFE).



5 **6**

7a R = R' = H **7b** R = R' = D
8a R = CH_3, R' = H **8b** R = CD_3, R' = H
9a R = R' = CH_3 **9b** R = CD_3, R' = CH_3

Methods and Results

The synthetic procedures used in the preparation of 1-chloro- (**5**), 1,4-dichloro- (**6**), and 1,4-dideuterio-7-norbornanol (**7b**) are outlined in Scheme 1.[8] 7-Norbornanol (**7a**), 1-methyl- and 1-methyl-d_3-7-norbornanol (**8a** and **8b**), and the 1,4-dimethyl derivatives **9a** and **9b**, respectively, were prepared following published procedures[9] using labeled precursors when necessary. The alcohols were converted to triflates and subjected to kinetic measurements as described in the Experimental Section. The results are presented in Tables 1 and 2.

Discussion

The most pronounced effect of bridgehead substitution on the solvolysis rate of 7-norbornyl triflate is the rate retardation (1/1700) caused by replacing one bridgehead hydrogen atom with chlorine. This can be ascribed to the inductive effect of chlorine acting from the β-position relative to the reacting center. In a recent paper, Kirmse and Schoen[5b] discussed different approaches to destabilized 7-norbornyl cations. *Inter alia* they have shown that 1-cyano-7-norbornyl brosylate is inert in dioxane–water mixtures even under forcing conditions (130 °C, 7 days). The corresponding triflate reacted under similar conditions and after 6 days afforded a mixture of three products (Scheme 2). However, the rate of solvolysis was not reported.

(4) (a) Wenke, G.; Lenoir, D. *Tetrahedron* **1979**, *35*, 489. (b) Dewar, M. J. S.; Schoeler, W. W. *Tetrahedron* **1971**, *27*, 440. (c) Sunko, D. E. *Croat. Chem. Acta* **1980**, *53*, 525.

(5) (a)Kirmse, W.; Streu, H-V. *J. Org. Chem.* **1985**, *50*, 4187. (b)-Kirmse, W.; Schoen, S. *Croat. Chem. Acta* **1992**, *65*, 551, and references therein.

(6) (a) Gassman, P. G.; Hornback, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 2487. (b) Gassman, P. G.; Hornback, J. M.; Marshall, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 6238. (c)Miles, F. B. *J. Am. Chem. Soc.* **1967**, *89*, 2388. (d) Miles, F. B. *J. Am. Chem. Soc.* **1968**, *90*, 1265. (e) Sunko, D. E.; Vančik, H.; Deljac,V.; Milun, M. *J. Am. Chem. Soc.* **1983**, *105*, 5364.

(7) (a) Sieber, S.; Schleyer, P. v. R.; Vančik, H.; Mesić, M.; Sunko, D. E. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1604. (b) Schleyer, P. v. R.; Sieber, S. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1606. (c) Sieber, S. *Dissertation*, Universität Erlangen-Nürnberg, 1993. (d) Mesić, M.; Sunko, D. E.; Vančik, H. *J. Chem. Soc. Perkin Trans. 2* **1994**, 1135.

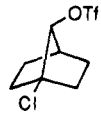
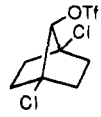
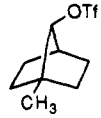
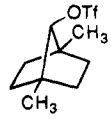
(8) (a) Dauben, W. G.; Chitwood, J. L.; Scherer, K. V. *J. Am. Chem. Soc.* **1968**, *90*,1013. (b) Lap, B. V.; Paddon-Row, M. N. *J. Org. Chem.* **1979**, *44*, 4979; see also Thomas, A. F. *Deuterium Labeling in Organic Chemistry;* Appelton-Century Crafts, New York, 1971.

(9) Kirmse, W.; Streu, J. *Synthesis* **1983**, 994.

(10) Gassman, P. G.; Talley, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 4138.

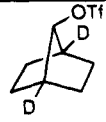
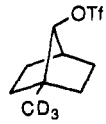
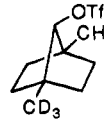
(11) Creary, X.; McDonald, S. R. *J. Org. Chem.* **1985**, *50*, 474.

Table 1. Rates of Solvolysis of Bridgehead Substituted 7-Norbornyl Triflates

	solvent (w/w % TFE)	t/°C	k/s^{-1}	k_{rel} at 45 °C
 **5-OTf**	80	100	$(9.45\pm0.05)\times10^{-6}$	
		45	4.61×10^{-9} [c]	5.86×10^{-4}
 **6-OTf**	80	119	$(1.15\pm0.12)\times10^{-5}$	
		100	$(1.35\pm0.11)\times10^{-6}$	
		45	6.58×10^{-10} [b]	8.36×10^{-5}
 **7a-OTf**	100	25	2.02×10^{-7} [a,b]	
	80	65	$(8.99\pm0.04)\times10^{-5}$	
		45	7.87×10^{-6} [b]	1.0
	70	25	$(6.75\pm0.03)\times10^{-7}$	
 **8a-OTf**	80	45	$(4.78\pm0.02)\times10^{-4}$	61
 **9a-OTf**	80	65	$(8.96\pm0.19)\times10^{-3}$	
		45	$(1.05\pm0.01)\times10^{-3}$	133

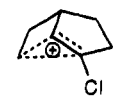
[a] Data from refs 10 and 11. [b] Calculated from data at other temperatures. [c] Calculated from data at 100 °C using calculated $\Delta H^{\ddagger}$ value for **6-OTf**.

Table 2. Deuterium Isotope Effects in the Solvolyses of 7-Norbornyl Triflates 7b–9b-OTf

	solvent (w/w % TFE)	t/°C	k_H/k_D
 **7b-OTf**	70	25	1.034 ± 0.008*
 **8b-OTf**	80	45	0.968 ± 0.003
 **9b-OTf**	80	45	0.968 ± 0.011

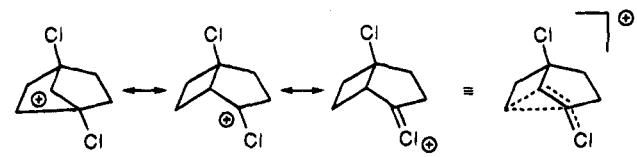
* $k_H = 6.770 \times 10^{-7}$ s^{-1}.

Since the main products were 5-cyano-2-bicyclo[3.2.0]-heptene and the unrearranged 1-cyano-7-norbornanol, the authors concluded that the ionization occurs with predominant participation of the C4–C5 bond, thus preferring intermediate **10** to **11**. The inverse situation prevails with the 1-chloro derivative **5-OTf** where chlorine exerts a resonance stabilizing and an inductively destabilizing effect (σ^{+}_{Cl} 0.04; σ^{+}_{CN} 0.67). With the former effect prevailing, the rate reduction for the chlorine derivative **5-OTf** relative to the parent compound is much smaller than with the cyano derivative. Consequently, **5-OTf** is expected to ionize to the intermediate cation **12**.



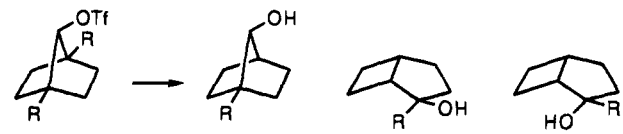
12

The only 7-fold rate reduction observed with the dichloro derivative **6-OTf** can best be rationalized by assuming the intervention of resonance structures **13a–c** which only slightly destabilize the transition state relative to the monosubstituted ion. Kirmse[5a] has also shown that



13a **13b** **13c**

bridgehead methyl substitution drastically changes the solvolysis product composition relative to the unsubstituted case. With one methyl group at C1, the products are almost totally rearranged 2-bicyclo[3.2.0]heptyl derivatives. This perturbation of the parent system makes

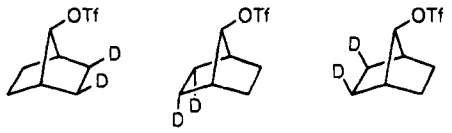


R = H	95 %		5 %	
R = CH_3	5.4 %	90.4 %		4.2 %

the Wagner–Meerwein rearrangement of the delocalized, unsymmetrical intermediate the main pathway. In the solvolysis reaction of the unsubstituted derivative, the cationic intermediate still retains most of the positive charge on C7, while with the methyl derivative more of the charge on C1 favors anchimeric assistance and participation of the C1–C6 σ-bond.

The effect of methyl substitution is a 60-fold increase of the reactivity of the respective triflate and the effect of a second methyl group is additive and not multiplicative. The observed 2-fold rate enhancement caused by the second methyl group is entirely due to the statistical factor. This shows that only one methyl group interacts with the cationic center and rules out a symmetrical but doubly delocalized, symmetry forbidden C_s structure for the rate-determining transition state.

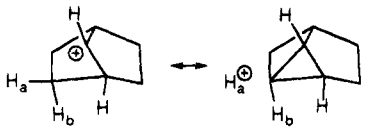
Interesting conclusions can be drawn from the kinetic behavior of the deuterium substituted derivative **7b-OTf**. Bridgehead deuterium substitution gives rise to a normal isotope effect of k_H/k_D 1.034 for two deuteriums. This effect confirms the theoretical prediction that the tilted structure of C_s symmetry (**3**), which is at the MP4(sdq,-fc)/6-31G**//MP2(full)/6-31G* level of theory,[7] 2.86 kcal mol^{-1} higher in energy than **1**, is the transition state in the solvolysis reaction.[7] In this structure the C1–H(D) bonding orbital is no longer in the nodal plane of the p-orbital at C7 as in the C_{2v} structure **2**, thus allowing some hyperconjugative overlap of the respective orbitals. At the highest level of theory, **2** is 2.5 kcal mol^{-1} less stable than **3**.[7] In the light of these results a reinterpretation of the origin of the reported γ-isotope effects[4d,6e] in 2,3-dideuterio-7-norbornyl triflates **15–17** is justified.



	15	16	17
k_H/k_D	1.038±0.009	1.006±0.024	1.024±0.007

The small normal isotope effect in the solvolysis of **15** is, we still believe, steric in origin. It is caused by nonbonding interactions of the leaving group and the *syn-exo* hydrogen (deuterium) atoms at carbon atoms 2 and 3 which are relieved in the transition state.[12] The isotope effects reported for **16** and **17** likely have their origin in homohyperconjugation of the C−H(D) pseudo π-orbitals of the methylene groups with the p-function at C7.

Homohyperconjugation is best described in terms of resonance structures **18** and **19**. In the canonic structure **19** the hyperconjugating hydrogen (H_a) should exert a normal γ-isotope effect, while the effect of the other hydrogen (H_b) should be unity or slightly inverse. An identical situation can be found in the paper by Saunders and Siehl,[13,14] who reported opposite effects for the *exo*- and *endo*-deuterium in the γ-deuterated delocalized cyclobutyl cation.



18 **19**

The 7-norbornyl cation is a rather unusual example of a case where the structure of the rate-determining transition state differs from the structure of the product determining intermediate. The transition state structure **3** of C_s symmetry prevents any significant stabilizing interaction with the ribbon orbitals[3,4] which is manifested by the extreme electron demand of the cationic center[15] and the low reactivity of 7-norbornyl derivatives. The subsequent bridge flipping mechanism leading to the 3.5 kcal/mol more stable intermediate ion of C_1 symmetry accounts for the formation of 95% of unrearranged products with retained configuration and of about 5% of rearranged 2-bicyclo[3.2.0]heptyl products.[1] The label scrambling reported by both Gassman[6] and Kirmse[5a] which interconvert the methylene hydrogen (deuterium) atoms arises from a bridge flipping involving transition structures **3** and **4** and intermediate delocalized cations **20** and **21**.

20 **21**

Deuterium substitution in the bridgehead methyl groups gives rise to an inverse γ-effect which can be compared with the similar effect on a deuterated non-migrating methyl group in the neopentyl system[16] (Table 3). Since in the neopentyl case the process is clearly k_Δ, the solvolysis of **8** is also likely k_Δ but with a more or less advanced bridging.

Scheme 2

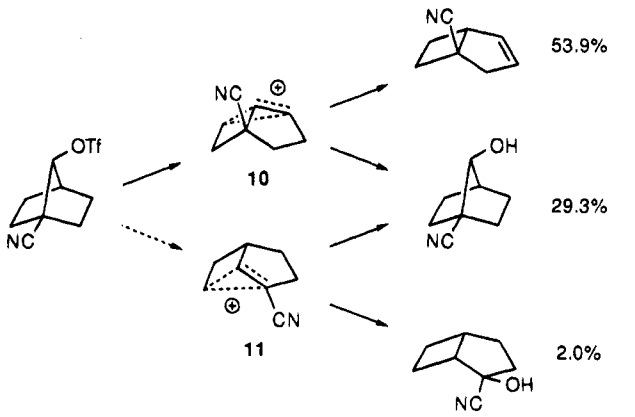
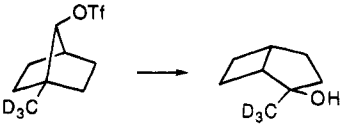
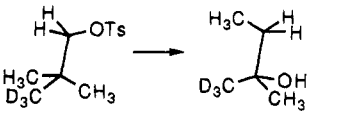
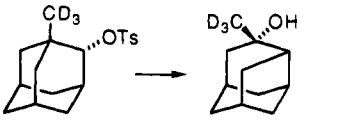


Table 3. γ-CD_3/CH_3 Isotope Effects

	% rearr	k_H/k_D
	92 (70A)	0.968 ± 0.003 (80T, 45°C)[a]
	100 (50E)	0.94 (80E)[b]
	33 (60D)	1.05 ± 0.01 (60D, 60°C)[c]

[a] This work. [b] Reference 16. [c] Reference 17.

In this context, the small but normal isotope effect from the γ-position in the solvolysis of 1-methyl-d_3-2-adamantyl tosylate (k_H/k_D = 1.05) reported by Majerski *et al.*[17] deserves a comment. This system probably involves internal return and rearrangement. The rearranged protoadamantyl structure (33% from product studies) should give a β-isotope effect in the normal direction of about 10%, but the 67% of unrearranged structure could give an inverse effect of about 0.98. A limited amount of internal return could make the effect even smaller. With the two effects acting in the opposite direction, the positive observed effect could ensue.

From these results it can be concluded that bridgehead substitution in 7-norbornyl derivatives shows solvolysis rate effects which can be expected on the basis of the delocalized, nonclassical structure for this cation which is supported by high level *ab initio* calculations. The *transition state* in the solvolysis reaction of parent system closely resembles the tilted classical ion of C_s symmetry where anchimeric assistance from the underlying ribbon orbitals of the six-membered ring as suggested by Hoffmann and Heilbronner[3] is negligible. Tilting the bridge

(12) For an example of such steric effects see: Badger, R. C.; Fry, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 1680.
(13) Saunders, M.; Siehl, H.-U. *J. Am. Chem. Soc.* **1980**, *102*, 6868.
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towards one side enables the symmetry-allowed stabilization of the cationic center with the C1–C2 σ-bond resulting in the delocalized structure **1** for the 7-norbornyl cation. Structure **1** accounts for all observed and reported rate and substituent effects and also for the structure and label distribution in the substitution products. The final solution of the 7-norbornyl cation problem was thus accomplished by a fruitful interplay of experiment and theory at the highest *ab initio* level.

Experimental Section

General. The purity of all compounds was examined by GC and TLC. Melting points are uncorrected. IR spectra were taken on a Perkin-Elmer 167 spectrometer. ^1H and ^{13}C spectra were recorded on JEOL FX 90 and Varian XL 300 spectrometers. Mass spectra were obtained on a Varian CH-7 spectrometer.

Synthetic Procedures. 1-Chloro-7-norbornanol (5). 1-Chloro-7,7-dimethoxynorbornane (0.35 g, 0.0018 mol) was isolated as a byproduct in a GC purification on a FFAP column of the reaction mixture obtained in the preparation of 7-norbornanol by the method analogous to the one for **7b**. The compound is a colorless oil: ^1H NMR ($CDCl_3$) δ 1.25–2.20 (m, 9H), 3.46 (s, 6H). The further conversion to 1-chloro-7-norbornanone (IR 1797 cm^{-1}) and its reduction to the alcohol gave 0.09 g (0.0006 mol) of the desired product. The procedures were the same as for the protio analog **7a**: total yield 34%; IR 3450 cm^{-1} (OH str); ^1H NMR ($CDCl_3$) δ 1.28–2.26 (m, 9H), 3.81 (s, 1H).

1,4-Dichloro-7-norbornanol (6). Starting from 1,4-dichloro-7-norbornanone[18] (3.16 g, 0.017 mol), we prepared the alcohol by a standard LAH reduction in dry ether: yield of sublimed material (50 °C, 14 mmHg), 1.92 g (60%); mp 78–80 °C; ^1H NMR ($CDCl_3$) δ 1.86–2.53 (m, 9H), 3.83 (s, 1H).

1,4-Dideuterio-7-norbornanol (7b). 1,4-Dichloro-7,7-dimethoxynorbornane (5 g, 0.022 mol) was deuterated in ethanol-*d* using the published procedure.[8a] Ethanol-*d* was prepared by reacting tetraethoxysilane with D_2O.[8b] The reaction was performed under dry nitrogen with sodium powder in dry ether. 1,4-Dideuterio-7,7-dimethoxynorbornane was purified by preparative GC on a FFAP column. Yield 1.0 g (51%). The further procedure was identical to the one described for the preparation of the protio analog **7a**:[18] total yield of the sublimed product 460 mg (18.4%); mp 157–159 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 3.991 (s, 1H), 1.847 (d, 2H), 1.550 (d, 2H), 1.489 (s, 1H), 1.278 (d, 2H), 1.168 (d, 2H); ^{13}C NMR (75.43 MHz, $CDCl_3$) δ 79.781 (d, J_{CH} = 151 Hz), 40.012 (t, J_{CD} = 21.3 Hz), 26.777 (t, J_{CH} = 136 Hz), 26.601 (t, J_{CH} = 136 Hz): 98% d_2 by mass spectrometry.

1-Methyl-7-norbornanol (8a). 2-Cyclopentenone (1.5 g, 0.019 mol) was converted in four steps to the desired alcohol as described in the literature:[9] yield 0.39 g (17%); mp 97–99 °C; MS *m/e* (%) 126 (5), 108 (65), 98 (3), 97 (4), 95 (10), 94 (4), 93 (100), 91 (2), 83 (5), 81 (5), 80 (7), 79 (10), 71 (5), 70 (10), 69 (5), 68 (5), 76 (12), 57 (10), 56 (5), 55 (12), 53 (6), 43 (7), 41 (15), 39 (8); IR 3340 cm^{-1} (OH str).

1-Methyl-d_3-7-norbornanol (8b). The synthetic procedure was identical as for **8a** but using CD_3I instead of CH_3I: total yield 20%.; MS *m/e* (%) 129 (18), 111 (100), 98 (30), 97 (10), 96 (55), 93 (48), 83 (28), 81 (10), 79 (20), 71 (11), 70 (19), 69 (10), 68 (5), 67 (11), 57 (12), 56 (10), 55 (11), 53 (8), 43 (21), 41 (25), 39 (18); IR 3340 cm^{-1} (OH str), 2230 cm^{-1} (CD str).

1,4-Dimethyl-7-norbornanol (9a). Starting from 3-methyl-2-cyclopentenone (1.25 g, 0.013 mol), we prepared the compound in four steps following the published procedure:[9] yield 0.32 g (18%); mp 20 °C; IR 3380 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (s, 6H), 1.30 (d, 2H), 1.25–1.70 (m, 6H), 3.15 (s, 1H).

1-Methyl-d_3-4-methyl-7-norbornanol (9b). The compound was prepared by the identical procedure as described for the protio derivative using CD_3I (>99% d_3) instead of CH_3I: ^1H NMR ($CDCl_3$) δ 1.00 (s, 3H), 1.30 (d, 2H), 1.25–1.70 (m, 6H), 3.16 (s, 1H).

Triflates 5–9-OTf were prepared using the published general procedure.[19] The purity was checked by IR and TLC.

Kinetic Measurements. For triflates **8a-OTf**, **8b-OTf**, **9a-OTf**, and **9b-OTf**, the previously described potentiometric rate measurement method was used.[20] The data were evaluated by an on-line coupled microcomputer using a nonlinear least-squares program. The solvolyses were followed up to 4 half-lives and on the average 6–7 separate runs for each compound were taken. The solvolysis rates for **5** and **6** were measured using the sealed ampoule technique and titrating aliquots taken in definite time intervals up to 6 half-lives. In all these cases the solvent was 80% (w/w) TFE.

For **7b-OTf**, the previously described[21] bipolar-pulse conductometric method was used to measure rates at 25 °C. The triflates at concentrations of 0.6–0.8 mM were solvolyzed in 70% (w/w) TFE (10–15 mL) for at least 2 half-lives and the data were analyzed using a doubly weighted least-squares program. To negate the long term effect of temperature variation both the unlabeled and labeled triflates were run simultaneously in two separate conductance cells.

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