The 7-Norbornyl Cation. Structure and Interactions

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Abstract: In an attempt to detect possibly hyperconjugative, homohyperconjugative and/or steric interactions in the title compound specifically deuterated 7-norbornyl triflates **3–8**-OTf were solvolyzed in aqueous trifluoroethanol. **3**-OTf and **4–6**-OTf showed normal, positive isotope effects ($k_H/k_D > 1$). The α-effect of 1.13 in **3**-OTf is interpreted as being due to incomplete rehybridization and strained geometry at C_7. γ-Effects were observed only in the exo-deuterated derivatives **4–6**-OTf ($k_H/k_D = 1.024$–1.10) and can be ascribed to a net relief of steric strain during the progression from initial state to activated complex. The absence of isotope effects in the solvolysis of endo-deuterated derivatives **7**-OTf and **8**-OTf precludes any hyperconjugative or neighboring bond interaction as the one implied in the nonclassical structure **2**. Products obtained under solvolytic conditions in solvents of different nucleophilicities and ionizing power show almost identical, predominantly ($\sim$90%) retained configuration. This result can be rationalized in terms of bent structures for the intermediate cation such as those predicted by MINDO calculations. A greater proportion of inverted products (up to 35%) is obtained under S_N2 conditions in aprotic solvents (DMF, benzene/18-crown-6). Here direct back-side displacement competes with a possible front-side attack on the sulfur atom of the leaving group. An alternative, but highly speculative mechanism involving pseudorotation cannot be dismissed.

Among secondary carbocations, the 7-norbornyl cation (**1**) stands out for its unusual properties. Its solvolytic precursors are extremely unreactive; the tosylate in acetic acid has a half-life of 3.35×10^6 years at 25 °C.[2] Attempts to generate **1** in Sb-F_5–SO_2 solutions failed due to its rapid rearrangement to the 2-norbornyl cation.[3] This rearrangement has not been observed under solvolytic conditions. Solvolysis at elevated temperature (at 205 °C in AcOH and at 100 °C in HCO_2H for 2 and 16 h, respectively) afforded $\sim$97% of unrearranged alcohol **1**-OH with predominantly ($\sim$90%) retained configuration.[4,5] The methyl/H and phenyl/H rate ratios of 7-norbornyl derivatives are among the highest known.[6–8] These observations together with the Hammett ρ value of -5.64[6] are taken as evidence for an enormously high electron demand of **1**.[9]

Quantum mechanical and molecular mechanical factors have been invoked to explain the destabilization of the 7-norbornyl cation. The $C_7C_1C_4$ angle of 93.7° in norbornane[10] is considered partly responsible for the solvolytic inertness of 7-norbornyl derivatives. This is in accordance with the Foote[11] and Schleyer[12] correlations. For comparison, 2-adamantyl tosylate which has a normal tetrahedral angle at C_2 solvolyzes 10^6 times faster than **1**-OTs.[13] Implied in this reasoning is the understanding that the cationic center in **1** is planar. When a C_{2v} symmetry was imposed on the carbon skeleton the planarity of the cationic center was also sustained by ab initio calculations.[14]

Chart I
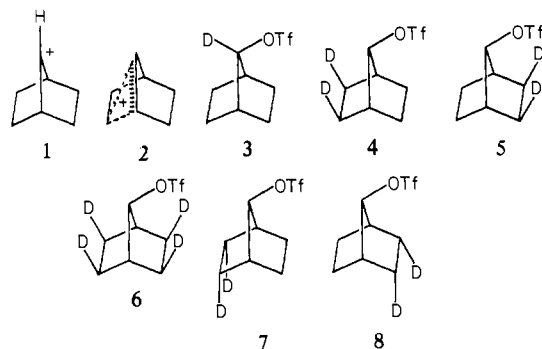
Electronic, quantum mechanical effects which could stabilize **1** also seem to be absent. Here two different interactions should be taken into account: (a) carbon–carbon hyperconjugation with the underlying cyclohexane ring skeleton[9] and (b) carbon–hydrogen homohyperconjugation with the pseudo-π orbitals of the methylene carbon–hydrogen bonds.[15] Symmetry arguments preclude hyperconjugative interaction with the degenerate set of ribbon orbitals of the σ bonds.[9] It is however this type of interaction, illustrated by the nonclassical cation **2**, which apparently has to be taken into account in order to rationalize both the formation of rearranged products with the bicyclo[3.2.0]heptane skeleton and the predominance of unrearranged products with retained configuration at C_7.[4b,5b] In order to find an answer to these questions we decided to carry out a detailed investigation of the solvolysis of specifically deuterated 7-norbornyl triflates **3–8**-OTf in a series of solvents of different nucleophilicities and ionizing power. The use of the more reactive triflates[16] has the advantage of working at lower temperatures (65 °C vs. 100 °C) than was the case in the earlier work with tosylates.[2] The specific aim was to search for hyperconjugative interactions mentioned above and to gain additional information on the geometry of the incipient cation **1**.

Methods and Materials

Synthetic Procedures. The alcoholic precursors of triflates **3–8** were prepared by using standard synthetic procedures described in detail in the Experimental Section. The endo-deuterated norbornanols **7**-OH and **8**-OH could not be separated but were used as a 1:1 mixture.

(1) (a) Taken in part from the Ph.D. Thesis of H.V., University of Zagreb, 1981. (b) Institute of Physics, University of Zagreb.

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Kinetic Measurements. In all cases, the previously described potentiometric rate measurement method has been used.[17] All substrates were solvolyzed in 80% (w/w) aqueous 2,2,2-trifluoroethanol for at least 2 half-lives and the data from 5 to 6 separate runs were evaluated by using a nonlinear least-squares program.

Solvolysis Product Studies. Details of the procedures used are given in the Experimental Section. All products were stable under the reaction conditions. The amount of retention was determined in acetone-d_6 solution by ^{1}H NMR when standards of known composition are used. Each FT analysis required 8 to 100 scans. The estimated error of this method is ±5%.

Experimental Section

All compounds were identified by IR, ^{1}H NMR, and MS. The following instruments were used: a Perkin-Elmer 167 IR spectrometer, Varian T-60 and Bruker WP-80DS (FT) NMR spectrometers, and a Varian CH7 mass spectrometer.

Kinetic measurements were carried out on a Radiometer-Kopenhagen SBR3 titrigraph coupled to an automatic titrator TTT2 with autoburette ABU11.

7-Deuterio-7-norbornanol (3-OH). 7-Norbornanone[18] (0.55 g, 4.87 mM) in dry ether (75 mL) was added to a solution of LiAlD$_4$ (1.89 g, 0.045 M) in ether (35 mL). After being stirred at room temperature for 2 h the mixture was worked up as usual. After the solvent was removed the product was purified by sublimation (70 °C 50 mm Hg). Yield 0.46 g (84%), mp 144-146 °C (lit. mp 154-156.5 °C),[19] 97% d_1 by mass spectrometry.

2,3-exo-Dideuterio-anti-7-norbornanol (4-OH). *anti*-7-Norbornenol[18,20] (1.25 g) in ethyl acetate (5 mL) was deuterated with deuterium gas at room temperature and atmospheric pressure in the presence of 300 mg of 10% Pd-on-charcoal catalyst. After the usual workup the crude product was purified by sublimation at 40 °C and 15 mm of pressure. Yield 960 mg (74%); mp 157-159 °C; 94% d_2 by mass spectrometry; IR 3300 (OH) 2870, 2950 cm^{-1} (CH), 2170, 2180 cm^{-1} (CD); ^{1}H NMR (CD$_3$COCD$_3$) δ 3.93 (s, 1 H), 3.65 (s, 1 H), 1.83 (s, 4 H), 1.3-1.05 (m, 4 H); ^{13}C NMR δ 79.5 (d, $J = 24$ Hz), 40.2 (d, $J = 14$ Hz), 26.8, 24.6 (m).

2,3-exo-Dideuterio-syn-7-norbornanol (5-OH). The preparation was performed according to the published procedure.[21] From 1 g of *syn*-7-norbornenol[19] after sublimation 750 mg (72%) of pure 5-OH was obtained: mp 157-159 °C; 97% d_2 by mass spectrometry; IR same as 4-OH; ^{1}H NMR δ 3.96 (s, 1 H), 3.65 (s, 1 H), 1.85 (s, 2 H), 1.76-1.1 (m, 6 H); ^{13}C NMR same as 4-OH.

2,3,5,6-exo-Tetradeuterio-7-norbornanol (6-OH). 7-Hydroxy-2,5-norbornadiene[22] (380 mg) was deuterated as described for 4-OH; 89.3% d_4 by mass spectrometry, mp 144-146 °C.

2,3-endo-Dideuterio-7-norbornanone (9). 7,7-Dimethoxynorbornenone[19] (1.0 g, 6.5 mM) dissolved in ethyl acetate (3 mL) was added with a syringe to a stirred suspension of 10% Pd/C catalyst (10 mg) in 5 mL of ethyl acetate in a hydrogenation apparatus filled with deuterium gas under atmospheric pressure. After the absorption of deuterium ceased, the catalyst was removed by filtration, and the solvent evaporated. To the oily residue 5% sulfuric acid (3.5 mL) was added and the mixture stirred for 24 h at room temperature. After extraction with pentane (3 × 5 mL) and drying over MgSO$_4$, the solvent was removed. The oily residue was recrystallized from petroleum ether; mp 75-77 °C; 97% d_2 by mass spectrometry; IR 2940, 2880, 2830 (CH), 2180 (CD), 1820, 1765, 1735 cm^{-1} (C=O); ^{1}H NMR δ 1.55-1.95 (m, 6 H), 1.15-1.30 (m, 2 H).

syn- and anti-endo-2,3-Dideuterio-7-norbornanol (7-OH and 8-OH). From 200 mg (1.70 mM) of 9 with 280 mg of LiAlH$_4$ in ether (20 mL) after the usual workup and sublimation was obtained 100 mg of a mixture of equal amounts of 7-OH and 8-OH which was directly converted to the corresponding triflates.

Product Studies. (a) In TFE, HFIP, and Aqueous Acetone. 4-OTf or 5-OTf (100 mg) was dissolved in 5 mL of solvent containing 0.5 mL of 2,6-lutidine. The mixture was heated in a sealed ampule for about 10 half-lives. Most of the solvent was distilled off over a 12-cm Vigreux column and pentane (20 mL) was added to the residue. The pentane solution was washed with ice cold diluted (1:1) HCl and with water.

Table I. Rate Constants and Isotope Effects for Solvolysis of 7-Norbornyl Triflates (3-8) in 80% (w/w) 2,2,2-Trifluoroethanol (TFE) at 65 °C

triflate	$k \times 10^5$ s^{-1}	$k_H/k_D{}^a$
3	7.95 ± 0.11^b	1.13 ± 0.02
4	8.78 ± 0.04	1.024 ± 0.007
5	8.66 ± 0.06	1.038 ± 0.009
6	8.17 ± 0.46	1.10 ± 0.06
7 + 8	8.89 ± 0.17	1.011 ± 0.024

^{a} Corrected to 100% deuterium content. ^{b} $k_H = 8.99 ± 0.04$.

After the solvent was removed, the residue was sublimed in vacuo (10 mmHg).

(b) In Acetic Acid. 4-OTf (160 mg) was dissolved in 7 mL of glacial acetic acid containing 30 mg of dry sodium acetate and 0.7 mL of acetic anhydride. The mixture was heated in a sealed ampule to 115 °C for up to 10 half-lives. Excess solvent was removed in vacuo (25 °C (10 mmHg)). After some water was added, the product was continuously extracted with pentane for 12 h. NaHCO$_3$ was added to the extracts to remove traces of acetic acid. After filtration the solvent was removed by distillation over a small column. The resulting 7-norbornyl acetate was dissolved in dry ether (5 mL) and the solution added to a stirred suspension of LiAlH$_4$ (200 mg) in ether. After the usual workup the ether solution was dried (MgSO$_4$) and evaporated and the residue sublimed in vacuo (10 mmHg).

(c) In Dimethylformamide. Commercial grade DMF was purified by stirring with dry Al$_2$O$_3$ under nitrogen. Subsequently it was dried over molecular sieve 4A. 4-OTf (100 mg) was dissolved in 5 mL of DMF and heated for 14 days to 100 °C. Solvent was removed in vacuo (10 mmHg) at 44 °C over a small column and the residue treated with water (8 mL). The product was extracted with pentane (4 × 3 mL). After the solvent was removed the residue was dissolved in dry ether (5 mL) and reduced with LiAlH$_4$. The reduction and workup were as described above.

(d) In Benzene.[23] 18-Crown-6 (46 mg) was dissolved in 5 mL of dry benzene. Dry potassium acetate (0.5 g) was added and the mixture vigorously stirred in an ampule for 30 min. 5-OTf (213 mg) was added and the ampule sealed and heated with stirring to 90 °C for 8 days. About 80% of the solvent was carefully removed by distillation, then water (3 mL) was added and the product taken up in ether. The ether solution was dried with MgSO$_4$ and reduced with LiAlH$_4$ (120 mg) as described above. The crude product was sublimed in vacuo (35 °C (10 mmHg)).

Results and Discussion

Isotope Effect Studies. The results of kinetic isotope effect measurements are presented in Table I.

α-Deuterium Isotope Effect and the Solvolysis Mechanism. The presence of an α-deuterium isotope effect is indicative for the dissociation mechanism.[24] Its magnitude reflects the degree of rehybridization at the reacting carbon atom and is related to different stages of ion-pairing and/or nucleophilic solvent assistance in the rate-determining step.

For the sulfonate leaving group a maximum effect of $k_H/k_D = 1.23$ has been observed and interpreted as involving rate-determining formation of the solvent-separated ion pair (k_2 rate determining).[24] Smaller effects ($\sim$1.15) occur when the tight ion pair is formed in the slow step (k_1 rate determining) and/or when the sp^3 → sp^2 rehybridization is incomplete.[24] Nucleophilic solvent assistance or neighboring group participation also reduces the magnitude of α-effects.[25]

Results of this and previously published studies indicate that the solvolysis of 7-norbornyl derivatives occurs similarly to that

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Table II. Mechanistic Criteria for the Solvolysis of Secondary Tosylates at 25 °C

R-OTs	Q'^a	m^b	$k_H/k_{\alpha\text{-}D}$	ref
2-adamantyl	1.0	1.0	1.23	29
7-norbornyl^c	1.01^d	1.03^d	1.15^e	this work
2-*endo*-norbornyl	0.60	0.69	1.21	29
menthyl	0.64	0.69	1.19	29

^{a} Q' is an adjustable blending parameter that reveals to what extent a given substrate approaches 2-propyl ($Q' = 0$) or 2-adamantyl ($Q' = 1$) in behavior.[29] ^{b} Calculated from the equation: $\log (k/k_0)_{\text{ROTs}} = m \log (k/k_0)_{\text{2-AdOTs}} = mY_{\text{OTs}}$. ^{c} Triflate. ^{d} Calculated from data for 80T, 100T and AcOH. ^{e} Extrapolated from higher temperature.

of 2-adamantyl derivatives[26] via the rate-determining formation of the solvent-separated ion pair. The observed reduced α-effect of 1.15 at 25 °C (1.13 at 65 °C) could be explained by a rate-determining formation of the tight ion pair, but this seems rather unlikely in view of the fact that product studies have shown that inversion of configuration—a consequence of tight ion-pair decomposition by rear-side solvent attack—does not constitute the major product-forming step (see Table III).

At this point in order to assess the importance of nucleophilic solvent assistance a comparison of the solvolytic behavior of **1-OTf** with other secondary substrates with the use of 2-adamantyl tosylate as standard is warranted. The compiled data are given in Table II.

The values for Q' and m support the contention that **1-OTf** behaves similarly as 2-adamantyl tosylate and that the solvolysis of this substrate is not influenced by solvent nucleophilicity. Thus the difference in the magnitude of α-isotope effects between these two substrates (1.15 vs. 1.23) cannot be caused by solvent effects or ion-pairing phenomena but in our opinion must have its origin in the peculiar geometry of **1**. Angle deformation at C_7 in the ground state results in an $sp^{2.46}$ hybridization of the C_7–H bond[27a] as contrasted by an sp^3 hybridization in 2-adamantyl derivatives. Vibrational changes associated with the carbonium ion formation and the corresponding α-effect are therefore expected to be smaller. A comparison of the calculated H/D fractionation factors for cyclobutane (1.40) and propane-*2-d* (1.50)[27b] lends further support to the argument that strained molecules because of a lowering of the vibrational frequencies for the C–H(D) bond should show smaller α-isotope effects. In conjunction with differences in hybridization in the ground state, a reduced α-effect could also arise from nonplanar cationic transition states[28] such as those predicted for the intermediate 7-norbornyl cation by MINDO calculations.

The γ-Isotope Effect. The γ-isotope effects in both *syn-* and *anti-*2,3-exo-dideuterio-7-norbornyl triflates are positive (1.038 and 1.024), with the difference between the two falling within the limits of error. The average effect for either of the isomers can be taken as the square root of the effect of the tetradeuterio derivative **6**, $(1.10)^{1/2} = 1.048$, which is in line with the magnitude of γ-effects observed in solvolyses of 1-adamantyl[30] and 2-adamantyl tosylates.[31] The latter effects were interpreted in terms of carbon–carbon hyperconjugation but the alternative carbon–hydrogen homohyperconjugative interaction as the origin of these

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Table III. Product Analysis from Solvolyses of 7-Norbornyl Sulfonate Esters in Protic Solvents

compd	solvent	$Y_{t\text{-BuCl}}$	temp, °C	react. time^a	% retention	ref
4-OBs	HCOOH	+2.05	100	16^b	85 ± 5	5b
4-OTf	80HFIP^c	+1.862	70	10	90 ± 5	this work
5-OTf	70TFE	+1.659	65	10	90 ± 5	this work
4-OBs	$50A^d$	+1.40	150	20^b	85 ± 5	5b
4-OBs	70MeOH	+0.96	150	20^b	80 ± 5	5b
5-OTf	80A	−0.67	60	10	90 ± 5	this work
5-OTf	AcOH	−1.639	80	1.5	90 ± 5	this work
4-OTf	AcOH	−1.639	115	10	90 ± 5	this work
4-OBs	AcOH	−1.639	205	1.5^b	90 ± 5	5b
5-OTf	90A	−1.86	230	10	90 ± 5	this work
4-OTf	80DMF		108	10	90 ± 5	this work

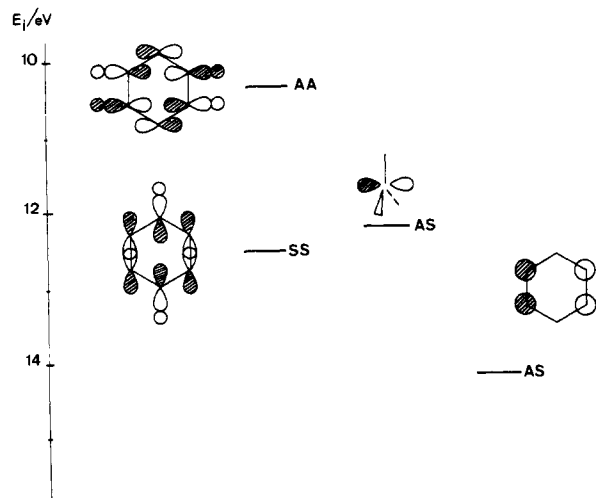^{a} Half-lives. ^{b} Hours. ^{c} 80% (w/w) 1,1,1,3,3,3-hexafluoro-2-propanol. ^{d} 50% (v/v) acetone.

Table IV. Product Analysis from Reaction of 4-OTf in Aprotic Solvents

solvent nucleophile	temp, °C	reaction time^a	% retention
DMF	100	14	65 ± 5
benzene 18-crown-6, KOAc	90	8	70 ± 5

^{a} Days.

effects could not be excluded.[30] In 7-norbornyl derivatives **4–6-OTf** the observed γ-effects cannot be ascribed to hyperconjugative interactions on the following grounds. In the planar symmetric (C_{2v}) cation interactions with the high-lying AA and SS ribbon orbitals (C–C hyperconjugation) are symmetry forbidden.[9] A homohyperconjugative interaction with the $4B_2$ orbital of the pseudo-π-type located at the methylene groups of the underlying six-membered ring (Figure 1) is improbable because of the large energy gap between these orbitals and the p orbital at C_7. This gap can be estimated to be about 2.9 eV as calculated from the first p-ionization potential of the carbon atom (11.26 eV)[32] and the ab initio value for the $4B_2$ orbital (14.15 eV).[33] However, the strongest argument against any kind of hyperconjugative interaction comes from the fact that γ-effects are absent in the corresponding endo-deuterated derivatives **7-OTf** and **8-OTf**. Since long-range hyperconjugative (CH or CC) interactions should necessarily affect the force constants of the respective CH or CC bonds and therefore give rise to secondary kinetic isotope effects,[30] the absence of these effects with the endo-deuterated derivatives **7-OTf** and **8-OTf** excludes any interaction of this kind.

Augmenting this reasoning is the comparison with the 2-norbornyl system where only in the 2-exo derivative's γ-effects were observed and they were of almost identical magnitude for both the 6-exo and 6-endo deuterio (d_1) derivatives.[34] Therefore the
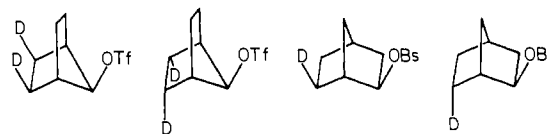
k_H/k_D 1.011 ± 0.024   1.024 ± 0.007   1.106 ± 0.018   1.084 ± 0.019

best rationalization for the observed γ-effects in the exo-deuterated derivatives **4-6-OTf** is offered by invoking a steric effect operating

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Figure 1. Orbital interactions in the 7-norbornyl cation.

between the exo hydrogens of the methylene groups and the substituents at C_7. A similar explanation has been suggested by Fry and collaborators for the γ-effects observed in solvolysis of 2-alkyl-2-adamantyl derivatives.[37] Here, as in the present case, the constraints placed on the vibrational freedom are more severe in the ground state than in the transition state, thus giving rise to "normal" isotope effects. If any significance can be attached to the fact that, although within the limits of error, all measured syn-exo-γ-effects were slightly larger than the anti-d_2 effects, the steric interpretation is also in accord with the ^{1}H NMR spectrum of 7-norbornanol which shows a downfield shift for the syn-exo hydrogens of 0.4 ppm relative to the anti-exo hydrogen atoms.

Stereochemistry of Solvolysis Products. The product studies were performed in five different protic solvent mixtures having Y values between -1.86 and $+1.862$ and two aprotic solvents (benzene and N,N-dimethylformamide). The results are presented in Table III and IV. The solvolysis in all protic solvents used resulted in a predominant retention of configuration. These results are in agreement with previously obtained data of Gassman[4] and Miles[5] for the solvolysis of **1-OTs** and **1-OBs** in other solvents and at higher temperatures (see Table III). They do not confirm the opinion[5] that the ratio of retained to inverted product is solvent dependent.

The fact that the stereochemical outcome of the solvolysis of 7-norbornyl sulfonates remains constant regardless of the fact that the ionizing power of the solvent differed in Y values for almost four powers of ten speaks strongly against the suggested notion[14] that solvation effects are responsible for the predominant retention of configuration at C_7. The origin of this phenomenon is to be sought in the peculiar geometry of the cation (see below). A possible direct displacement on the sulfur atom of the triflate leaving group can be ruled out on the basis of the observed α-isotope effect. Since rear-side-solvent participation can be excluded, inversion of configuration at C_7 in the solvolysis reaction could occur by bridge flipping of the bent structure in competition with front-side collapse of the solvated cation.[14b]

The stereochemistry of the substitution products was also studied in two aprotic solvents, DMF and benzene. In polar DMF no external nucleophile was present but after a certain reaction time the formed immonium ion was quenched with water.[38] In nonpolar benzene as solvent and in the presence of 18-crown-6 "naked" acetate[23] was the only nucleophile. In both cases a greater proportion of inverted product was formed. This can be ascribed
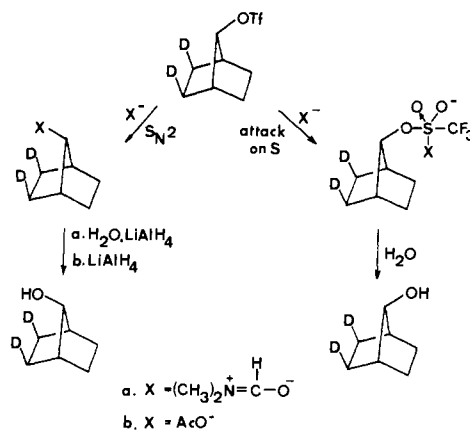
to a direct displacement reaction on the unionized substrate. The use of aqueous DMF gives results which are identical with those in protic solvents.

The mechanism of the retention reaction in aprotic solvents is more difficult to assess. A direct front-side displacement on carbon is forbidden because of the unfavorable HOMO–LUMO interaction.[39] However, in analogy to vinyl triflates[40] it is is reasonable to assume that retained configuration in the products might result from nucleophilic attack on sulfur. Such an attack was shown to occur in methanol with methoxide and cyanide as nucleophiles, but was not expected to occur in acetic acid buffered with acetate.[41]

It remains to be seen why, assuming an attack on sulfur, almost identical results were obtained by two different nucleophiles under quite different reaction conditions.

One could also speculate about other mechanisms such as the long sought after pseudorotation of a pentacovalent carbon intermediate[42] for which 7-substituted norbornyl derivatives would be particularly good substrates. Further experiments are required to solve this mechanistic detail. From the available experimental evidence, Scheme I can account for the results obtained in nonpolar solvents under S_N2 conditions.

Comparison with Quantum Mechanical Calculations; the Geometry of the 7-Norbornyl Cation. Quantum mechanical calculations give different geometries for the 7-norbornyl cation. While ab initio procedures prefer the symmetrical (C_{2v}) structure, MINDO/2, MINDO/3, and EH calculations produce unsymmetrical geometries.[14]

The following arguments can be put forward against the symmetrical C_{2v} structure. The preferential retention of configuration in a range of solvents of different nucleophilicities and ionizing power is in opposition to the known behavior of planar carbocations. If products were formed from the tight ion pair, depending on solvent nucleophilicity different and much larger amounts of inverted products should be obtained. Product formation from the solvent-separated ion pair should, in a planar cation, give different amounts of inverted and retained products in the range

Scheme I

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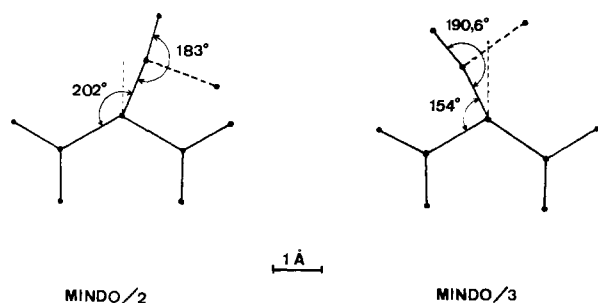
MINDO/2   MINDO/3

Figure 2. Head-on drawings of the 7-norbornyl cation with indicated approximate positions of the leaving group in the transition state.

a rapid equilibrium between the two bent structures.

of solvents used, which is obviously not the case. Finally, the formation of rearranged products of the bicyclo[3.2.0]heptyl structure cannot be brought in accord with the symmetry of the ribbon orbitals.[9] The noninteraction with these orbitals precludes any σ-bond delocalization as implied in the nonclassical structure **2** if the intermediate ion or the transition state leading to it retains the C_{2v} symmetry.

The results of the present investigation can be rationalized by assuming that the structure of the transition state leading to the 7-norbornyl cation is unsymmetrical in concord with the semiempirical MINDO calculations.

The presently available experimental evidence is insufficient for deciding which of the two bent MINDO structures should be preferred. As can be seen from a head-on drawing (Figure 2) steric, nonbonded interactions with the exo hydrogen (deuterium) atoms are stronger on each one of the sides (syn or anti) for the bent structures than for the ab initio structure. The tilting of the bridge also allows for some interaction of the p orbital with the SS-ribbon orbital on one side of the ion, thus allowing for the formation of a small amount of bicyclo[3.2.0]heptane products. However, this interaction cannot be significant in the rate-determining transition state as it would give rise to a hyperconjugative γ-effect in both endo- and exo-deuterated triflates **4–8**. Since, as Gassman[4] has observed, of the two isomeric rearrangement products **9** and **10** derived from **4** isomer **9** is the major product, the MINDO/3 structure is a better candidate for the explanation of the rearrangement reaction. An equally acceptable explanation can be provided by a bridge-flipping mechanism or
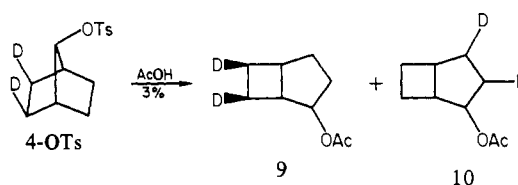
Conclusions

On the basis of the results obtained in the course of this work, one can conclude the following:

(1) Electronic interactions of hyperconjugative origin as implied in the nonclassical structure **2** of the 7-norbornyl cation could not be observed.

(2) Secondary deuterium γ-effects of positive value ($k_H/k_D >$ 1) if present as in **4-6-OTf** are not caused by carbon–hydrogen homohyperconjugation but are of steric origin. In some other cases, as in 1- and 2-adamantyl derivatives,[30,31] they could be ascribed to carbon–carbon hyperconjugation.

(3) The solvolysis of **1-OTf** is not assisted by solvent and solvent effects are not responsible for the predominant retention of configuration at C_7 in solvolyses of 7-norbornyl derivatives.

(4) Accumulated experimental evidence gives preference to the unsymmetrical structure of the incipient 7-norbornyl cation (and the transition state leading to it) as predicted by MINDO calculations.

(5) Products of retained configuration obtained in aprotic solvents under S_N2 conditions can arise from two alternatively possible but still speculative mechanisms: (a) nucleophilic attack on sulfur or (b) pseudorotation on a pentacovalent intermediate.

Chiral Deuterium Labeling: New Method for Determination of Rotational Propensities

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Abstract: Determination of internal rotational propensities in thermal rearrangements of cyclic compounds has, in the past, involved the use of optical activity as a tracer and has required usually arduous correlation of configurations between the educt and products by chemical means. Replacement of this method by introduction of a chiral, diastereomeric deuterium hydrogen methylene group permits configurational relations to be established by NMR—either ^{2}H NMR or ^{1}H NMR alone or with LIS enhancement. As a first application of the new method, the relative rotational propensity, R_A, of the cyano and isobutenyl groups in 1-cyano-2-isobutenyl-2,3-dideuteriocyclopropane has been determined to be 3.9 ± 0.5.

Internal rotational propensity is the key to many types of not obviously concerted thermal rearrangements. Specifically in rearrangements of cyclopropanes and cyclobutanes, an internal rotational component determines the stereochemistry of automerization and ring enlargement.[1-7]

In the past, investigation of this factor has employed optical activity as a tracer. Relatively straightforward in clarifying the

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