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$$D = \left(\frac{\pi RT}{M}\right)^{1/2} \left(\frac{a}{2}\right) \left[\frac{PV}{RT} - 1\right]^{-1}$$

for values of P in the range of observed values for solvent internal pressure (P_i). This expression is approximated by a form very similar to eq 9.
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Cyclopropyl Triflates. Neighboring-Group and Solvent Effects

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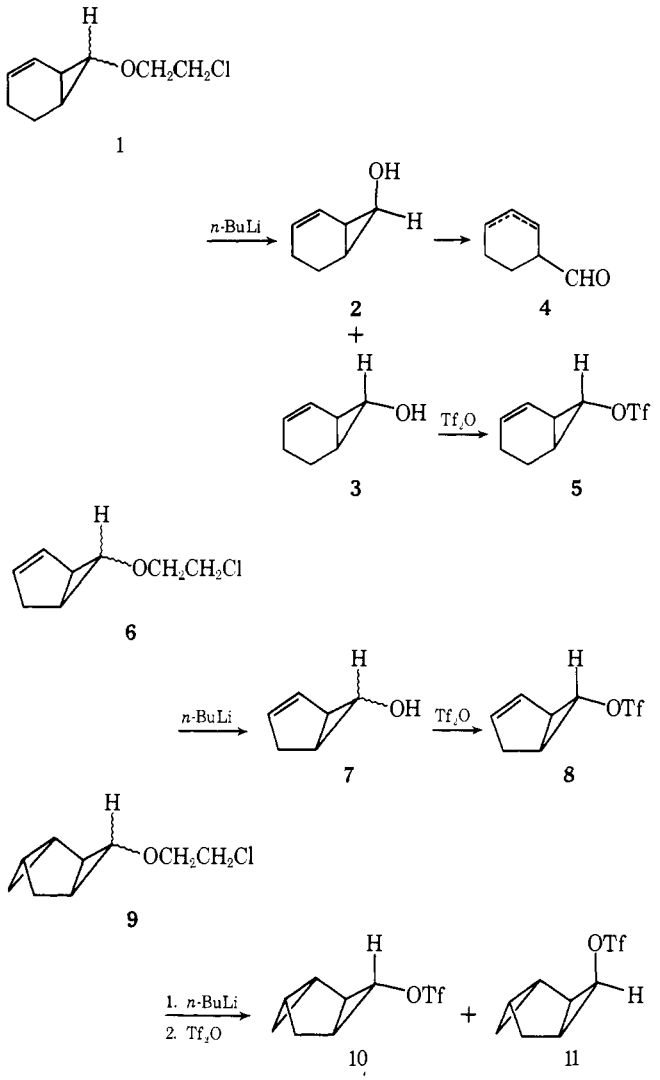
Abstract: Buffered acetolysis of *exo*-bicyclo[3.1.0]hex-2-en-6-yl triflate (**8**) and *exo*-bicyclo[4.1.0]hept-2-en-7-yl triflate (**5**) suggests an olefin-assisted ionization in the former and competing "normal" and olefin-assisted ionization in the latter. Proposed intermediates are the bicyclo[2.1.1]hex-2-en-5-yl cation (**21**) in the ionization of **8** and the 7-norbornenyl cation (**17**) along with partially opened allylic cation **14** in the acetolysis of **5**. A solvent study indicates very little response to solvent ionizing power in a series of cyclopropyl triflates, which undergo ionization leading to a wide variety of cationic intermediates. Winstein–Grunwald m values lie in the range of typical nucleophilic solvolyses. These results are interpreted in terms of decreased demand for solvent stabilization of trifluoromethanesulfonate anion and a transition state with little charge development.

Cyclopropyl triflates undergo ionization, leading to transition states and intermediates with varying amounts of allylic cationic character.[1] Recently we observed an ionization in which the first cationic intermediate is essentially cyclopropyl in character.[2] When a neighboring group was appropriately situated, anchimeric assistance to ionization was observed. The key factor which allowed these observations was the fusion of a small ring to the exo cyclopropyl triflate, which prevented the allowed electrocyclic ring opening. As part of a study of the requirements for neighboring-group participation to incipient cyclopropyl cations, we have prepared *exo*-bicyclo[4.1.0]hept-2-en-7-yl triflate (**5**), *exo*-bicyclo[3.1.0]hex-2-en-6-yl triflate (**8**), and the cyclopropyl analogue of **8**, *trans*-tricyclo[4.1.1.$0^{2,4}$]hept-*exo*-3-yl triflate (**10**). It was thought that in these systems, electrocyclic opening during ionization would be sufficiently blocked so as to allow the observation of neighboring-group participation by the appropriately situated group. As part of a general mechanistic investigation, the effect of solvent ionizing power[3] (Y) on solvolyzing cyclopropyl triflates was determined. We report here the results of these studies.

Results and Discussion

Preparation of Cyclopropyl Triflates 5, 8, 10, and 11. The desired cyclopropyl triflates were prepared essentially using procedures developed by Schöllkopf.[4] Reaction of the olefins 1,3-cyclohexadiene, cyclopentadiene, and bicyclo[3.1.0]hex-2-ene[5] with dichloromethyl β-chloroethyl ether and methyllithium led to the expected β-chloroethyl cyclopropyl ethers **1**, **6**, and **9**, respectively, as a mixture of exo and endo epimers. Cleavage of **1** with n-butyllithium gave an alcohol mixture from which only *exo*-bicyclo[4.1.0]hept-2-en-7-ol (**3**) could be isolated. The *endo*-bicyclo[4.1.0]hept-2-en-7-ol (**2**) underwent facile rearrangement to give a mixture of 2- and 3-cyclohexenecarboxaldehyde (**4**). This facilitated separation of the two isomers and allowed the preparation of pure *exo*-bicyclo[4.1.0]hept-2-en-7-yl triflate (**5**), uncontaminated with the endo epimer.

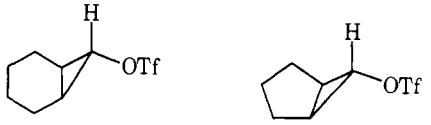
The addition of β-chloroethoxy carbene to cyclopentadiene gave a mixture of β-chloroethyl cyclopropyl ethers **6** enriched in the endo epimer. Cleavage of this mixture with n-butyllithium gave an alcohol mixture which was treated directly with a solution of trifluoromethanesulfonic anhydride in pyridine. An exothermic reaction ensued and upon workup, no trace of *endo*-bicyclo[3.1.0]hex-2-en-6-yl triflate could be detected. This is attributed to the probable high reactivity of this *endo*-cyclopropyl triflate, which can undergo concerted ionization and ring opening to a cyclohexadienyl cation, with concomitant release of the stain energy associated with the bicyclo[3.1.0]hex-2-en-6-yl system. This "self destruction"



of the triflate corresponding to endo alcohol **7** allowed preparation of exo-bicyclo[3.1.0]hex-2-en-6-yl triflate (**8**), uncontaminated with the endo epimer.

The reaction of dichloromethyl β-chloroethyl ether with methyllithium and bicyclo[3.1.0]hex-2-ene gave a mixture of epimers with the endo isomer of **9** predominating. Cleavage of the β-chloro ethers **9** with butyllithium gave an alcohol mixture which we were not successful in separating. Conversion of the alcohol mixture to the corresponding triflates **10** and **11** was accomplished in the usual manner. The isolation of **11** was unexpected in view of the anticipated high reactivity of an *endo*-cyclopropyl triflate fused to a cyclopentyl system[1a] and borne out by the observed inability to isolate the analogous endo-bicyclo[3.1.0]hex-2-en-6-yl triflate. The ratio of endo triflate **11**/exo triflate **10** was 1.9:1.

Acetolysis of *exo*-Bicyclo[4.1.0]hept-2-en-7-yl Triflate (11). Table I gives rate data for buffered acetolysis of **5, 8,** and **10** along with saturated analogues **12** and **13.** These saturated

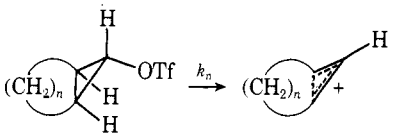


derivatives have been postulated to ionize by a mechanism assisted kinetically by partial fragmentation of the internal cyclopropane bond.[1a,6] This process leads to a "partially-opened allylic cation" and will be termed k_n, the normal ionization mode. The k_n term is a σ-assisted rate and is *not* a measure of the unassisted rate of ionization of **12** and **13.** It

Table I. Rates of Solvolysis in Acetic Acid–0.1 M Sodium Acetate

Compd	Temp, °C	k, s^{-1}	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu	k_{rel} (100 °C)	k_{unsatd}/k_{satd}
5	100.0	$(1.23 \pm 0.01) \times 10^{-5}$	28.5	-5.2	107	0.02
	125.0	$(1.47 \pm 0.02) \times 10^{-4}$				
8	100.0	$(1.56 \pm 0.02) \times 10^{-5}$	29.6	-1.8	136	136
	125.0	$(2.04 \pm 0.02) \times 10^{-4}$				
10	160.0	$(6.13 \pm 0.03) \times 10^{-5}$[a]				0.11[b]
12	60.0	$(7.50 \pm 0.03) \times 10^{-6}$	26.3	-3.16	5191	
	80.0	$(7.65 \pm 0.01) \times 10^{-5}$				
	100.0	$(5.97 \pm 0.02) \times 10^{-4}$				
13	100.0	1.15×10^{-7}[c]			1	

[a] Solvent was 60:40 v/v acetone/water. [b] Value refers to k_{10}/k_{13}. Rate of 13 was $(5.67 \pm 0.02) \times 10^{-4}$ s^{-1} at 160 °C in 60:40 v/v acetone/water. [c] Extrapolated value. Data of Su. Sliwinski, and Schleyer, ref 1c.

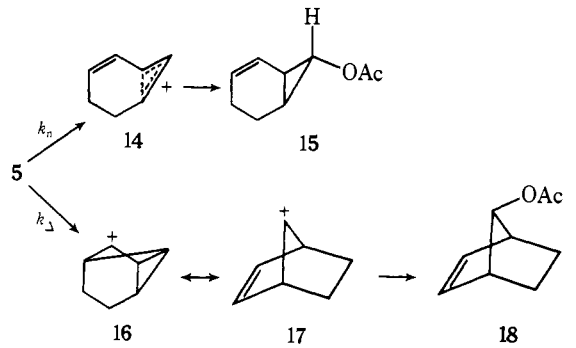


$n = 3, 4$

should be noted that the amount of assistance in the k_n process is larger for **12** than for **13.** Because of the difficulty associated with evaluating "unassisted" rates of solvolysis of **12** and **13,** no attempt will be made to do so. However unassisted rates of **12** and **13** should be of comparable magnitude.

Consider first the acetolysis of *exo*-bicyclo[4.1.0]hept-2-en-7-yl triflate (**5**). Solvolysis in buffered acetic acid gave a 90% yield of a 2.28:1 mixture of *exo*-bicyclo[4.1.0]hept-2-en-7-yl acetate (**15**) and *anti*-7-norbornenyl acetate (**18**). The mechanism shown in Scheme I is suggested to account for the

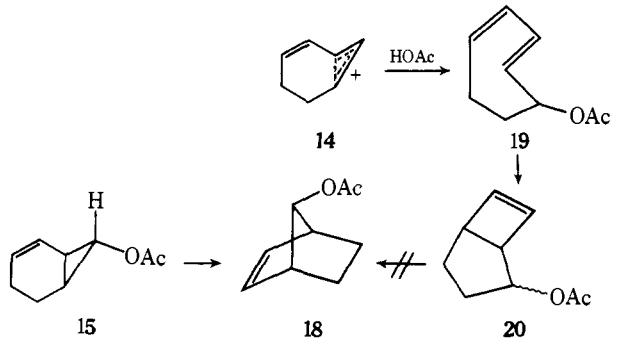
Scheme I



observed products. The rearranged acetate **18** is proposed to arise via the k_{Δ} process,[7] which leads to the 7-norbornenyl cation (**17**). Competing with this process is the k_n process, which leads to the retained acetate **15.** The product ratio would indicate that the two processes are of comparable magnitude.

In order to verify that *anti*-7-norbornenyl acetate (**18**) arose via olefinic participation in **5,** other mechanistic possibilities must be considered. Two such possibilities are shown in Scheme II.[8] If partially opened ion **14** were to capture solvent at the allylic position,[10] acetate(s) **20** could result (via **19**). Although tosylate derivatives in this system are known to give *anti*-7-norbornenyl acetate,[11] this rearrangement of **20** to **18** has been ruled out. Acetates **20** are stable under the reaction conditions.[12] The thermally allowed sigmatropic rearrangement of **15** to **18** is also ruled out, since **15** is likewise stable under the reaction conditions. In fact, preliminary studies show that a temperature in the order of 250 °C is required to initiate rearrangement of **15.**

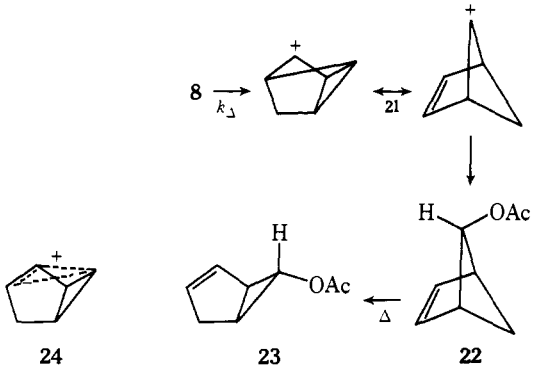
Scheme II



In terms of rate, *exo*-bicyclo[4.1.0]hept-2-en-7-yl triflate (**5**) solvolyzes 50 times slower than its saturated analogue **12.** A destabilizing inductive effect of the β-olefinic linkage is the origin of this rate reduction relative to **12.** The k_n process for ionization of **5** must therefore be of lower magnitude than the comparable k_n process for **12.** Consider next the k_Δ process suggested for **5.** Product data indicates that the k_Δ and k_n processes are of comparable magnitude. From product and rate data, the value of k_Δ is 0.38×10^{-5} s^{-1}. To adequately access the meaning of this value, it is necessary to compare this process to the rate in the absence of any participation. The unassisted rate of solvolysis of **12** should be a measure of such a process. In the absence of electrocyclic opening, the formation of an unopened cyclopropyl cation is expected to be extremely slow.[6] Therefore, the k_Δ process must be quite significant relative to an "unassisted" ionization of **5.**

Acetolysis of *exo*-Bicyclo[3.1.0]hex-2-en-6-yl Triflate (8). The data in Table I suggests that acetolysis of triflate **8** is enhanced by olefinic participation. This k_Δ process results in an unsaturated to saturated rate ratio (**8**/**13**) of 136 despite the electron-withdrawing inductive effect of the olefinic bond in **8.** However acetolysis of **8** gave *exo*-bicyclo[3.1.0]hex-2-en-6-yl acetate (**23**) as the sole product. This is the product predicted on the basis of a nonanchimerically assisted ionization (k_n process) leading to a partially opened allylic cation. Any mechanistic suggestion should account for both the anchimerically assisted rate and the observed product;[13,14] such a mechanism is shown in Scheme III. π participation leads to

Scheme III



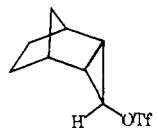
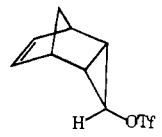
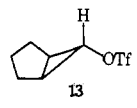
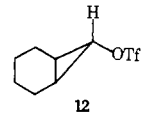
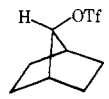
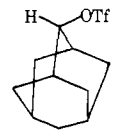
the bicyclo[2.1.1]hex-5-yl cation (**21**). More delocalized structures such as **24** cannot be supported or ruled out with the available data. Solvent capture of **21** leads in principle to acetate **22,** which is known to thermally rearrange to acetate **23.**[15] In the acetolysis of **8,** product analysis does not allow differentiation between the k_n and k_Δ processes. However, in the absence of π participation, the acetolysis rate of **8** is expected to be less than that of the saturated analogue **13,** due to the olefinic inductive effect. Measured rates, therefore, indicate that the k_Δ process (1.56×10^{-5} s^{-1}) is the major pathway followed.

The effect of the olefinic linkages in **5** and **8** may initially seem contradictory. Rates of **5** and **8** differ by only a factor of 1.3, while the saturated analogues, **12** and **13,** differ by a factor of 5191. The olefinic effect is to decrease the rate of **5** relative to the saturated analogue, but to increase the rate of **8** relative to the saturated analogue. These results are not inconsistent when one considers the fact that saturated analogues **12** and **13** are not good models for the unassisted solvolysis rates of **5** and **8.** Examination of rate data shows that the k_Δ processes are of comparable magnitude for both **5** and **8** (slightly larger for **8**). The effect of the double bond in **8** is to increase the rate so that the k_n process is kinetically unimportant. In **5** the effect is to decrease k_n so that the k_Δ process now becomes important. The significant feature is that anchimeric assistance, i.e., a measure of k_Δ relative to the "unassisted" rates of solvolysis of **5** and **8,** is of comparable magnitude in both **5** and **8.** The effect of the double bond is, therefore, largely rate enhancing (relative to unassisted rates) in both cases, although simple comparisons with saturated analogues do not reveal this.

Complete separation of exo triflate **10** from the endo epimer **11** was not successful. Solvolytic studies were carried out in the higher ionizing, less acidic, 60% aqueous acetone medium rather than in acetic acid because of the high temperature required for convenient rates. Titration data revealed that after a few minutes at 160 °C, none of the endo isomer **11** remained. Since the solvolysis rates of **10** and **11** are therefore drastically different, it was possible to determine rates of **10,** starting with a mixture of the two isomers **10** and **11.** In contrast to *exo*-bicyclo[3.1.0]hex-2-en-6-yl triflate (**8**), the cyclopropyl analogue **10** solvolyzes 9.2 times slower than *exo*-bicyclo[3.1.0]-hex-6-yl triflate (**13**). This may be attributed to a rate-retarding inductive effect of a nonparticipating β-cyclopropyl group. This effect makes triflate **4** the slowest ionizing secondary triflate thus far recorded.[16] The inductive β-cyclopropyl effect is also in accord with the relatively low reactivity of endo triflate **5,** which allows its observation.

Solvent Effects. Rate and product data on solvolysis of triflates **24** and **25** imply grossly different intermediates are involved during ionization.[2] Whereas **24** was suggested to give an unopened cyclopropyl cation as the initial cationic intermediate, **25** underwent an olefinic-assisted ionization which led to structurally rearranged products. In order to verify the presence of cationic intermediates in the ionization of **24** and to rule out diradical processes similar to those seen in the solvolysis of bicyclo[2.1.0]pent-5-yl derivatives,[17] a solvent effect study was carried out. The effect of solvent ionizing power[3] (Y) was determined in the system acetone/water. Data are given in Table II. The unusually small rate change (only a factor of 2.9) in changing from 80 to 60% aqueous acetone suggested little charge development in the transition state for the solvolysis of **24.** The corresponding m value of 0.32 is in the range of the usual nucleophilic solvolyses seen for primary substrates.[3] The unsaturated triflate **25,** which is postulated to ionize with olefinic participation, gave a similar low response to changing solvent ionizing power. We therefore sought to determine a "normal" m value to be expected in such systems. Rate behavior of *exo*-bicyclo[3.1.0]hex-6-yl triflate (**13**) was determined in the acetone/water medium. The m value of 0.26 for **13** shows that the response of triflates **24** and **25** to solvent ionizing power is not unusual for *exo*-cyclopropyl triflates fused to a small ring system. Indeed, cyclopropyl triflate itself (**26**), which gives a fully opened allylic cation as the first cationic intermediate, gives an m value of only 0.30.[21] Triflate **12** gives a value of 0.46, while the tertiary 1-methyl cyclopropyl triflate (**27**) gives a value of 0.38. A low response to solvent ionizing power, therefore, appears to be quite normal for cyclopropyl triflates regardless of the degree of allylic or cyclopropyl cation character in the initially formed cationic intermediate. Significant nucleophilic solvent assistance cannot

Table II. Rates of Solvolysis in Aqueous Acetone

Compd	Solvent[a]	Temp, °C	k, s^{-1}	m
 24	A	130.0	$(1.49 \pm 0.03) \times 10^{-4}$	0.32
	B	130.0	$(5.17 \pm 0.02) \times 10^{-5}$	
 25	A	90.0	$(1.87 \pm 0.02) \times 10^{-4}$	0.32
	B	90.0	$(6.58 \pm 0.04) \times 10^{-5}$	
 13	A	140.0	$(9.62 \pm 0.03) \times 10^{-5}$	0.26
	B	140.0	$(4.02 \pm 0.03) \times 10^{-5}$	
 26	A	70.0	$(4.02 \pm 0.00) \times 10^{-4}$	0.30
	B	70.0	$(1.47 \pm 0.02) \times 10^{-4}$	
 12	A	60.0	$(6.68 \pm 0.03) \times 10^{-4}$	0.46
	B	60.0	$(1.43 \pm 0.01) \times 10^{-4}$	
 27	A	24.7	$(3.81 \pm 0.09) \times 10^{-3}$	0.38
	B	24.7	$(1.07 \pm 0.04) \times 10^{-3}$	
 28	A	80.0	$(5.67 \pm 0.01) \times 10^{-4}$	0.57
	B	80.0	$(8.47 \pm 0.03) \times 10^{-5}$	
 29	B	25.4	$(1.73 \pm 0.02) \times 10^{-2}$	0.60
	C	25.4	$(4.11 \pm 0.05) \times 10^{-3}$	
	D	25.4	$(1.27 \pm 0.06) \times 10^{-3}$	

[a] A, 60:40 v/v acetone/water; B, 80:40 v/v acetone/water; C, 90:10 v/v acetone/water; D, 95:5 v/v acetone/water.

account for the variety of products formed in solvolyses of the substrates described. The structural rearrangements which these cyclopropyl substrates undergo are best explained in terms of limiting mechanisms. Thus in a series of triflates undergoing ionization leading to a variety of cationic intermediates, the m value criterion fails as a tool for mechanistic diagnosis.

The 2-adamantyl system has been proposed as a standard for limiting solvolyses in secondary systems.[18] To determine the origin of the low response to solvent ionizing power shown by cyclopropyl triflates, the m value for 2-adamantyl triflate (**29**) was determined. Although quite reactive, 2-adamantyl triflate (**29**) can be prepared. The solvent effect study gives an m value of 0.60 in this model system. This compares to a value of 0.91 for 2-adamantyl tosylate and 1.03 for the bromide in aqueous alcohol solvent.[18] An even lower value (0.57) is obtained for 7-norbornyl triflate (**28**).

What, then, is the origin of the low m values seen in the ionization of the cyclopropyl triflates shown in Table II? Data on the 2-adamantyl system suggests that the trifluoromethanesulfonate leaving group is at least in part responsible. Employing the triflate leaving group leads to a reduction in m value relative to the corresponding tosylate. The decrease is from 0.91 to 0.60 for the adamantyl system. This is consistent with the expected smaller solvent stabilization requirements of the unusually stable trifluoromethanesulfonate anion. Also in line with this reasoning is the m value of 1.03 for 2-adamantyl bromide. Bromide ion, being a poorer leaving group than sulfonates, should require greater solvent stabilization. The further decrease in m value in cyclopropyl triflates relative to the standard 2-adamantyl system may reflect the intrinsic instability of such incipient carbocationic systems. The m value for 7-norbornyl triflate is only 0.57, a value slightly lower than in the standard system. If the transition state leading to the initial cationic intermediate has less than "normal" charge development, a decreased response to solvent ionizing power is expected. The lower than normal m value in cyclopropyl triflates may, therefore, reflect less than "normal" transition-state charge development (an "early" transition state) as well as decreased solvent involvement with the leaving group. These findings are consistent with the work of Ong and Robertson.[22] An unusually low value of the temperature coefficient of enthalpy of activation ($\Delta C_p^{\ddagger}$) was found for the hydrolysis of *cis*- and *trans*-2-vinylcyclopropyl bromides. This was interpreted in terms of low transition-state charge development. It therefore appears that some of the criteria for establishing SN1 type mechanisms in solvolyses of cyclopropyl substrates fail due to the early transition state with its less than normal charge development.

Experimental Section

NML spectra were recorded on a Varian A-60A spectrometer and are reported in δ (parts per million) relative to tetramethylsilane. Mass spectra were recorded on an AEI Scientific Apparatus MS902 spectrometer. Infrared spectra were recorded on a Perkin-Elmer Infracord spectrometer.

Preparation of 5. *exo/endo*-7-(β-Chloroethoxy)bicyclo[4.1.0]hept-2-ene (1) was prepared in the usual manner[4] using 10 g of dichloromethyl β-chloroethyl ether, 45 g of 1,3-cyclohexadiene, and 102 ml of 1.24 M methyllithium. The yield of **1** was 8.07 g (76%), bp 63–67 °C (0.3 mm). The mass spectrum of **1** shows *m/e* 172.0634, 174.0590; calcd for $C_9H_{13}ClO$, *m/e* 172.0655, 174.0625. Cleavage of this mixture was accomplished in the usual manner using 2.0 g of **1** and 20 ml of 2.4 M butyllithium. The crude product mixture showed aldehydic protons at δ 9.70 (br s, 3-cyclohexenecarboxaldehyde, 1 part) and 9.62 (d, J = 1.3 Hz, 2-cyclohexenecarboxaldehyde, 3.3 parts). Distillation gave 0.446 g of *exo*-bicyclo[4.1.0]hept-2-en-7-ol (**3**), bp 50°C (0.2 mm): NMR (CCl_4) δ 6.2–5.2 (2 H, m), 3.63 (1 H, s), 3.30 (1 H, t, J = 2 Hz), 2.3–1.2 (6 H, m). No trace of endo alcohol **2** could be seen.

Triflate **5** was prepared from 0.404 g of a crude alcohol mixture and 1.9 g of trifluoromethanesulfonic anhydride in 7 ml of pyridine. The yield of **5** was 0.335 g (37%), bp 52–54 °C (1.1 mm): NMR (CCl_4) δ 6.3–5.5 (2 H, m), 4.25 (1 H, br s), 2.4–1.3 (6 H, m). The mass spectrum of **5** showed *m/e* 242.0049; calcd for $C_8H_9F_3O_3S$, *m/e* 242.0224.

Preparation of 8. A solution of 2 g of *exo/endo*-6-(β-chloroethoxy)bicyclo[3.1.0]hex-2-ene (**6**)[4] in 20 ml of ether was cooled to 0 °C and 20 ml of 2.3 M butyllithium in hexane was added dropwise over a 10-min period. After stirring at 15 °C for 10 min, the solution was cooled to −78 °C. Water was slowly added and the mixture was allowed to warm to room temperature. The organic phase was separated, dried over anhydrous sodium sulfate, filtered, and the solvents were removed in vacuo. The residue was distilled to give 0.55 g (45%) of a mixture of *exo*- and *endo*-bicyclo[3.1.0]hex-2-en-6-ol, bp 45–50 °C (1.0 mm). The mixture consists of mostly endo alcohol, which shows a triplet at δ 3.56, J = 7 Hz, in the NMR spectrum.

Trifluoromethanesulfonic anhydride (3.6 g) was added dropwise to 12 ml of cold pyridine. The mixture of exo and endo alcohols obtained above (0.55 g) was added to the cold, stirred solution. After storing at 0 °C for 12 h, the mixture was taken up into ether and water. The aqueous phase was extracted with an additional portion of ether and the combined ether extracts were washed with dilute hydrochloric acid, brine, and dried over anhydrous sodium sulfate. The solvent was removed by distillation through a Vigreux column and the residue was distilled through a short-path condenser at 5 mm. Triflate **2** (0.168 g; 13% based on starting alcohol mixture) was obtained as a colorless liquid: NMR (CCl_4) δ 6.0–5.45 (2 H, m), 3.66 (1 H, br s), 2.85–2.4

(3 H, m), 2.3–1.9 (1 H, m). The mass spectrum of **8** shows *m/e* 227.9947; calcd for $C_7H_7F_3O_3S$, *m/e* 228.0068.

Preparation of 10 and 11. A mixture of 9 g of bicyclo[3.1.0]hex-2-ene[5] and 3.2 g of dichloromethyl β-chloroethyl ether was cooled in an ice bath, while 38 ml of 1.08 M methyllithium (prepared from methyl iodide) in ether was added over a 10-min period. The mixture was stirred at room temperature for 20 min, cooled in an ice bath, and water was carefully added. The organic phase was separated, dried over anhydrous sodium sulfate, filtered, and the solvents were removed under vacuum. The residue was distilled to give 2.27 g (67%) of a mixture of exo and endo chloroethers **9**, bp 45–47 °C (0.2 mm): NMR (CCl_4) δ 3.15 (t, J = 6.5 Hz, cyclopropyl proton of endo isomer), 2.86 (t, J = 1.5 Hz, cyclopropyl proton of exo isomer). The ratio of exo/endo isomers was 0.3:1. The mass spectrum of **9** shows *m/e* 172.0619, 174.0536; calcd for $C_9H_{13}ClO$, *m/e* 172.0655, 174.0625.

A solution of 2.2 g of exo and endo chloro ethers **9** prepared above and 20 ml of ether was cooled in an ice bath, while 22 ml of 2.4 M butyllithium in hexane was added dropwise over a 10-min period. The mixture was then stirred at room temperature for 20 min, cooled to −78 °C, and 20 ml of water was added. The remainder of the workup was as previously described. The crude product was distilled to give 1.097 g (78%) of a mixture of exo and endo alcohols, bp 43–50 °C (1.1 mm): NMR (CCl_4) δ 3.30 (t, J = 6.5 Hz, cyclopropyl proton of endo isomer), 2.95 (t, J = 1.5 Hz, cyclopropyl proton of exo isomer), 3.05 (1 H, s, exchanges with D_2O). The ratio of endo/exo alcohol was 4:1.

Trifluoromethanesulfonic acid (2 g) was dissolved in 10 ml of cold pyridine and 0.60 g of the mixture of exo and endo alcohols described above was added. The mixture was stored at −10 °C for 12 h and then worked up as previously described. The solvent was removed by distillation through a Vigreux column with the last traces being removed under vacuum. The residue was distilled to give 0.466 g (35%) of a mixture of triflates **10** and **11**, bp 45–47 °C (0.7 mm). The mixture darkened on storage at −10 °C: NMR (CCl_4) δ 4.40 (t, J = 6.5 Hz, cyclopropyl proton of **11**), 3.97 (br s, cyclopropyl proton of **10**) 2.3–1.75 (3 H, m), 1.6–0.95 (3 H, m), 0.85–0.40 (1 H, m), 0.14 (1 H, q, J = 4 Hz). The ratio of **11**/**10** was 1.9:1.

Preparation of 12. *exo*-Bicyclo[4.1.0]hept-7-ol was prepared as described.[19] Conversion to the triflate **12** was accomplished in the usual manner in 70% yield, bp 57–59 °C (1.0 mm). NMR (CCl_4) δ 4.10 (1 H, t, J = 2 Hz), 2.10–1.0 (10 H, m).

Preparation of 27. 1-Methylcyclopropanol was prepared by the method of DePuy.[20] Trifluoromethanesulfonic anhydride (3.67 g) was dissolved in 20 ml of cold pyridine and 0.75 g of 1-methylcyclopropanol was slowly added to the cold solution. The mixture was kept at −5 °C for 4 h. The usual workup was employed and carried out rapidly using ice cold aqueous solutions. The cold organic extract was dried over anhydrous magnesium sulfate, filtered, and the solvent removed by distillation through a Vigreux column. The last traces of solvent were removed under vacuum. The residue was distilled to give 1.237 g (58%) of triflate **27**, bp 44–47 °C (25 mm). For kinetics, samples of **27** were redistilled immediately before use: NMR (CCl_4) δ 1.77 (3 H, s), 1.60–1.10 (2 H, m), 1.05–0.60 (2 H, m).

Preparation of 29. Trifluoromethanesulfonic anhydride (1.9 g) was dissolved in 10 ml of pyridine and the mixture was cooled to −5 °C. 2-Adamantanol (0.8 g) was added with stirring and the mixture was stored at approximately −10 °C for 2 h. The mixture was rapidly worked up in the usual manner using two pentane extracts and ice water. All manipulations were carried out rapidly with cold solutions. The organic phase was dried over anhydrous sodium carbonate, filtered, and the solvents were removed under vacuum. The crude liquid residue (0.72 g, 48%) was stored at −10 °C and used as soon as possible. Addition of a weighed sample of **28** to 80% aqueous acetone, followed by titration of liberated trifluoromethanesulfonic acid with standard sodium hydroxide indicated 89–92% purity: NMR (CCl_4) δ 5.92 (1 H, br s), 2.4–1.4 (14 H, m).

Kinetic Procedure. The kinetic procedure for runs in acetic acid is described elsewhere.[2] Kinetics in aqueous acetone solvents were carried out as follows for triflates **12**, **13**, **24**, **25**, **26**, and **28**. A 60:40 v/v acetone/water solution was prepared by mixing 60.30 g of 99.5% acetone with 50.25 g of distilled water. Triethylamine (1.012 g) was diluted to 100 ml with this solution and the resulting 0.10 M triethylamine solution was used for kinetics. An 80:20 v/v acetone/water solution was used for kinetics. An 80:20 v/v acetone/water solution was prepared by mixing 80.0 g of 99.5% acetone with 25.27 g of water. A 0.10 M triethylamine solution was prepared using this solution. The kinetics procedure was the same as in acetic acid, except the unreacted triethylamine was titrated with 0.02 M hydrochloric acid. For triflates **26** and **28**, weighed amounts of triflate were diluted with known quantities of triethylamine (less than 1 equiv) in the appropriate solvent system. The time was recorded for the triethylamine to react, as determined by monitoring the pH. Rate constants were calculated from the percentage reaction as a function of time. Rate constants given represent an average of at least five determinations at different percentage reaction. In the case of triflate **29**, initial amounts of triflate were calculated from weighted amounts on the basis of the known purity of **28**.

Solvolysis of 5. Product Analysis. A 0.162-g sample of triflate **5** was dissolved in 11 ml of 0.1 M sodium acetate in acetic acid containing 1% acetic anhydride. The mixture was heated (sealed tube) at 120 °C for 24 h and then taken up into ether and water. Gas chromatographic analysis on 4-ft, 10% SE 54 on Chromosorb P column at 100 °C shows two products. Samples of each were isolated by preparative gas chromatography. The major product of longer retention time was identical by infrared and NMR spectral comparison with an authentic sample of *exo*-7-acetoxybicyclo[4.1.0]hept-2-ene (**15**), prepared by reaction of the alcohol with acetyl chloride/pyridine in ether. The minor product of shorter retention time was identical by infrared and NMR spectral comparison with an authentic sample of *anti*-7-norbornenyl acetate (**18**). The yields of acetates **15** and **18** were determined in a separate run by gas chromatography, using dimethyl adipate as an internal standard.

Preparation of 15. Alcohol **3** (0.446 g) was added to a slurry of 0.7 g of acetyl chloride and 0.85 g of pyridine in 15 ml of ether. After stirring for 12 h, the mixture was poured into water and worked up in a standard manner. Distillation gave 0.412 g (67%) of *exo*-bicyclo[4.1.0]hept-2-en-7-yl acetate (**15**), bp 55 °C (0.7 mm): NMR (CCl_4) δ 6.2–5.8 (1 H, m), 5.7–5.3 (1 H, m), 3.95 (1 H, t, J = 2 Hz), 2.2–1.3 (9 H, m, sharp s at δ 1.93).

Solvolysis of 8. Product Analysis. A 0.170-g sample of triflate **8** was dissolved in 11 ml of 0.1 M sodium acetate in acetic acid containing 1% acetic anhydride. The mixture was heated (sealed tube) at 110 °C for 60 h, poured into water, and extracted with two portions of ether. After a standard workup, solvents were removed by distillation through a Vigreux column and the residue was distilled through a short-path condenser to give 0.0598 g (58%) of a product whose NMR spectrum is identical with that reported[15] for *exo*-6-acetoxybicyclo[3.1.0]hex-2-ene (**23**). Except for a small amount of a lower boiling impurity, the product was homogeneous by gas chromatography.

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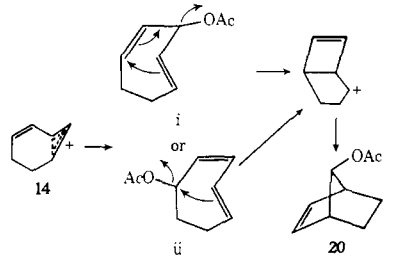
(8) A referee has suggested that the observed kinetic results are a result of a double bond less well aligned for conjugation in the six-membered ring of **5** than in the five-membered ring of **8**. To account for the rearranged product **18** from **5**, he has suggested plausible schemes shown below. We



cannot experimentally rule out these schemes as we have ruled out those in Scheme II. Neither can we rule out a stepwise rearrangement of **14** to the 7-norbornenyl cation **17**. However, rapid solvent (acetic acid) addition across the highly strained trans olefinic linkage[9] of i or ii would be expected (See ref 9 concerning reactivity of trans cycloolefins) in contrast to ion-

ization of I or ii, which employs the poor acetate leaving group. Without experimental verification, however, we cannot dismiss this possibility.

(9) E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Am. Chem. Soc.*, **87**, 934 (1965); (b) E. J. Corey, M. Tada, R. LaMahieu, and L. Libit, *ibid.*, **87**, 2051 (1965); (c) P. E. Eaton and K. Lin, *ibid.*, **87**, 2052 (1965); (d) G. H. Whitham and M. Wright, *J. Chem. Soc. C*, 891 (1971).

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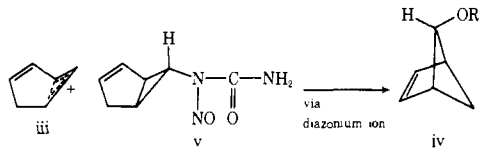
(13) A referee has suggested that partially opened cation iii, which receives vertical stabilization due to the double bond, could account for the observed



rates and products. This intermediate remains a possibility in the acetolysis of **8**, in which the forcing conditions necessary for solvolysis precluded isolation of **22**. However iii alone cannot account for the formation of products with the bicyclo[2.1.1]hex-2-en-5-yl ring system (iv) in the decomposition of *N*-nitroso-*N*-*exo*-bicyclo[3.1.0]hex-2-en-6-yl urea[14] (v). Our suggestion, as a result of the solvent effect study, is that the transition state for solvolysis of cyclopropyl triflates occurs quite early along the reaction coordinate. As such, little nuclear motion will have occurred and the major stabilization of this transition state is probably vertical. However, we believe that in the first cationic intermediates, derived from the k_Δ processes for ionization of **5** and **8**, there is significant nuclear reorganization.

(14) Products of this ring structure and rearranged ring structure have been observed in the decomposition of *N*-nitroso-*N*-*exo*-bicyclo[3.1.0]hex-2-en-6-yl urea: see W. Kirmse and F. Scheidt, *Angew. Chem., Int. Ed. Engl.*, **10**, 263 (1971). Similar intermediates have been proposed, but data does not allow evaluation of the extent of neighboring-group participation.

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(16) A complete product analysis study of solvolysis products from **10** was not undertaken due to the contamination of **10** with endo isomer **11**, the inability to produce large amounts of **10**, and the expected instability of the alcohol products at the temperatures necessary for solvolysis.

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(21) An *m* value of 0.45 has been reported for cyclopropyl triflate (**26**) in aqueous ethanol solvents: see P. Schleyer, W. F. Sliwinski, G. W. Van Dine, U. Schöllkopf, J. Paust, and K. Fellenberger, *J. Am. Chem. Soc.*, **94**, 125 (1972).

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Effect of Surfactant Micelles on the Stereochemistry and Rate of "Amsylate" Solvolytic Displacement Reactions in Water[1]

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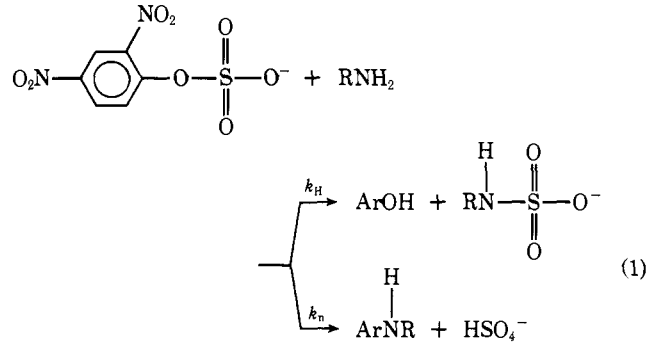
Abstract: A study of the effect of micelles on the aqueous solvolysis of alkyl *p*-trimethylammonium benzenesulfonates ("amsylates") has revealed that anionic micelles strongly inhibit the rate, and in some cases modify the stereochemistry, of the reaction. The mechanism of these solvolyses has been examined in detail. The results suggest that the rate inhibition is due to the squeezing out of water from the Stern layer of the mixed cationic–anionic micelles involved and the stereochemical changes are due to direct attack of the surfactant head group upon the reactive amsylate carbon atom, leading to a short-lived covalent dialkyl sulfate intermediate.

Though the first record of catalysis by surfactants dates back to 1906,[3a] the fact that micelles were the catalytically active species was not recognized until 1942[3b,c] and detailed investigations of micellar catalysis did not emerge until the late 1950's. Thus, the growth of micelle-related research during the past 20 years has been quite spectacular. Fortunately, the field has recently been the subject of numerous review articles[4a–d] and books.[4e,f]

Most chemical studies have concentrated on the effect of micelles on reaction rates and very few attempts have been made to look at the effect micelles might have in altering reaction products. The synthetic chemist has shown limited interest,[5] despite the recent impressive developments in phase-transfer catalysis.[6] To date only a few systems have been examined in which a micellar medium has been shown to affect the partitioning of an organic reaction. For example, in studying the competitive hydrolysis and aminolysis of aryl sulfates, Fendler et al.[7] were able to use cationic micelles of hexadecyltrimethylammonium bromide (CETAB) to alter the balance between k_n and k_H (eq 1). Under nonmmicellar conditions C–O bond cleavage (k_n) accounts for 75–98% of the observed reactions. They found that cationic micelles can induce "complete suppression of aniline formation".[7] The authors acknowledged the micelle's ability to alter the relative extent of competing reactions, but as an explanation suggested only that "[The above effects] may be primarily due to changes in the micro-environment of both the substrates and the transition states by a contribution of electrostatic and hydrophobic interactions".[7]



(1)

A second example of the use of micelles to alter a delicate balance between reaction pathways is found in the effect of micellization on the stereochemistry of alkyl amine deamination reactions.[8] It is argued[8a] that the diazotic acid reaction