

An analytical sample was prepared by three recrystallizations from dichloromethane-ether, mp 184–186 °C. Anal. (C<sub>22</sub>H<sub>29</sub>NO) C, H.

**20-Carbonitrile-3-methoxy-20-peracetoxy-19-norpregna-1,3,5-(10)-triene (31).** The procedure described for the preparation of **15** was repeated using 323 mg of **30** to afford, after chromatography on two silica gel plates in 1:3 hexane-dichloromethane, 235 mg (60%) of **31**: *R<sub>f</sub>* 0.51; IR (KBr) 5.59 (C=O) and 6.22 μ (aromatic); NMR (CDCl<sub>3</sub>) δ 0.98 (s, 3, C-18 angular CH<sub>3</sub>), 1.78 (s, 3, C-21 CH<sub>3</sub>), 2.04 (s, 3, COCH<sub>3</sub>), 3.78 (s, 3, OCH<sub>3</sub>), and 6.55–7.35 (m, 3, aromatic H); mass spectrum (70 eV) *m/e* (rel intensity) 397 (13), 354 (17), 337 (36), 323 (20), 312 (39), 271 (100) 227 (21), 199 (22), 186 (15), 173 (58), 160 (28), and 147 (37).

An analytical sample was prepared by three recrystallizations from ether-dichloromethane, mp 146–148 °C. Anal. (C<sub>24</sub>H<sub>31</sub>NO<sub>4</sub>) C, H.

**18-Carbonitrile-3-methoxy-19-norpregna-1,3,5(10)trien-20-one (33).** A solution of 161 mg (0.41 mmol) of **31** in 1.6 ml of dry degassed benzene in a quartz test tube was irradiated for 2 h. The solvent was evaporated, and the product was chromatographed on a silica gel plate in 1:20 ethyl acetate-dichloromethane to afford 53 mg (39%) of **33**: *R<sub>f</sub>* 0.60; IR (KBr) 4.48 (C≡N), 5.88 (C=O), and 6.22 μ (aromatic); NMR (CDCl<sub>3</sub>) 2.33 (s, 3, COCH<sub>3</sub>), 3.78 (s, 3, OCH<sub>3</sub>), and 6.50–7.35 (m, 3, aromatic H); mass spectrum (70 eV) *m/e* (rel intensity) 337 (61), 312 (23), 252 (27), 173 (20), 147 (14), 91 (14), and 84 (100).

An analytical sample was prepared by two recrystallizations from ether-dichloromethane, mp 215–217 °C. Anal. (C<sub>22</sub>H<sub>27</sub>NO<sub>2</sub>) C, H.

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## Homoallylic Participation in Cyclohexen-4-yl Tosylate

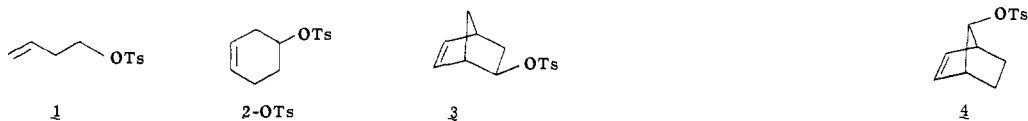
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**Abstract:** In hydroxylic solvents (HOS) the major substitution solvolysis product of cyclohexen-4-yl tosylate (**2-OTs**) has the same structure as the starting material, with tosylate replaced by -OS. The stereochemistry of this pathway can be determined by stereospecifically replacing one of the protons at the 5-position with deuterium and following the stereochemical relationship between the 4-proton and the remaining 5-proton by NMR. Inversion at the 5-position is taken to indicate solvent displacement, and retention to indicate some form of homoallylic assistance. Mixed stereochemistry can indicate either multiple pathways or a free carbonium ion mechanism. In this manner we have learned that aqueous 1,4-dioxane reacts with complete inversion, acetic acid with 17% retention, formic acid with 40% retention, and hexafluoro-2-propanol with complete retention. Thus the highly nucleophilic aqueous medium reacts entirely by solvent displacement. In acetic acid the homoallylic process has only just begun to compete observably with solvent displacement, in formic acid it has not quite reached the point of equal importance, and in the highly ionizing HFP it has become the sole mechanism.

Homoallylic participation may be defined as the assistance of a nonconjugated, unsymmetrically disposed double bond in the departure of a leaving group.<sup>2</sup> The fundamental acyclic, monocyclic, and bicyclic systems for observation of this phenomenon are, respectively, allylcarbonyl (**1**), cyclo-

hexen-4-yl (**2**), and *exo*-2-norbornenyl (**3**). The process should be distinguished from that in the fully symmetrical case with equivalent 1,3- and 1,4-overlap, as in the bishomocyclopropenyl ion produced from *anti*-7-norbornenyl tosylate (**4**). The ion



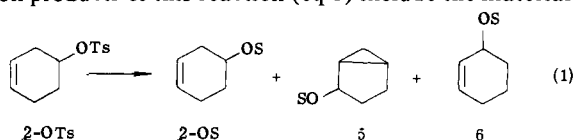
**Table I.** Solvent Properties and Reaction Rates at 77 °C

Solvent	$Y^a$	$N^a$	$k, {}^b s^{-1}$	$k, {}^c s^{-1}$
70% 1,4-dioxane/H <sub>2</sub> O	0.0	0.0	$1.3 \times 10^{-4}$	$1.8 \times 10^{-4}$
Acetic acid	-0.61	-2.35	$1.0 \times 10^{-4}$	$1.5 \times 10^{-4}$
Formic acid	3.04	-2.35	$7.2 \times 10^{-3}$	$6.0 \times 10^{-3}$
Trifluoroethanol	1.83	-2.79	$1.5 \times 10^{-4}$	$1.8 \times 10^{-4}$
Hexafluoro-2-propanol	3.61	-4.81	$3.1 \times 10^{-4}$	$8.6 \times 10^{-4}$

<sup>a</sup> Values from F. L. Schadt and P. von R. Schleyer, *Tetrahedron Lett.*, 2335 (1974). <sup>b</sup> Cyclohexen-4-yl tosylate. <sup>c</sup> Cyclohexyl tosylate.

produced by homoallylic participation, as from 1–3, has much weaker 1,4-overlap (if present at all) than 1,3-overlap.

The bicyclic system (3) is relatively well understood. Participation is extremely weak, so that the double bond actually causes a rate retardation.<sup>3</sup> Introduction of methyl groups on the double bond significantly increases homoallylic participation.<sup>4</sup> The acyclic system (1) has not been fully studied, although participation has been suggested on the basis of solvent effects.<sup>5</sup> The present investigation is concerned with the monocyclic system, cyclohexen-4-yl tosylate (2-OTs). The substitution products of this reaction (eq 1) include the material

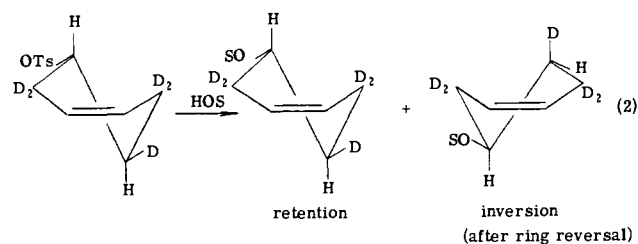


with the structure corresponding to the starting material (2-OS), the bicyclic material (5), and the hydride shift material (6).<sup>6</sup> Elimination products comprise more than half of the acetolysis product, but less in other solvents. We will be concerned only with the substitution component. Hanack et al.<sup>2b</sup> reported a small rate acceleration (cyclohexen-4-yl vs. cyclohexyl) and a small amount of the bicyclic product (5) in the acetolysis of 2-OTs and concluded that homoallylic participation is important. Wiberg et al.,<sup>7</sup> however, reported a modest rate deceleration for 2-OTs and concluded that homoallylic participation is small or absent. Because of the fundamental role of the cyclohexen-4-yl system in the field of homoallylic participation and the lack of agreement as to the extent of participation, we have carried out a detailed study of the solvolysis of cyclohexen-4-yl tosylate.

In our hands<sup>8</sup> cyclohexen-4-yl tosylate acetolyzed slightly more slowly than cyclohexyl tosylate. Although this kinetic criterion does not support participation, neither does it exclude it, because of the inductive rate retarding effect of the double bond. Furthermore, although a small amount of homoallylically rearranged product (5) has been observed,<sup>6</sup> the major substitution product has the same structure as the starting material (2-OS in eq 1). Thus the kinetic and product data do not yield a clear mechanistic conclusion concerning the presence of homoallylic participation in the solvolysis of 2.

We have chosen to use a stereochemical approach, similar to that applied to the solvolysis of cyclohexyl tosylate.<sup>9</sup> At the first level of consideration, solvent displacement ( $k_s$ ) on cyclohexen-4-yl tosylate (probably on an ion pair) should occur with inversion of configuration at the 4-position to give the major product, 2-OS, and homoallylic participation ( $k_\Delta$ ) followed by opening of the homoallyl intermediate should occur with retention of configuration to give the same material. Thus, in theory, product stereochemistry should give a quantitative separation of the reaction pathways. Because of rapid half-chair ring reversal, however, the substrate offers no diastereomeric handle. We have followed the stereochemistry of the reaction by use of a deuterated derivative. Introduction of any sort of substituent other than an isotope to make the diastereomeric differentiation can lead to significant changes in the structure of the transition state.

The derivative we chose is cyclohexen-4-yl-3,3,5,6,6-*d*<sub>5</sub> tosylate. The deuterium atoms at the 3- and 6-positions are present only to simplify the NMR spectrum. The 4-proton and the remaining 5-proton comprise an AB system, the coupling constant of which is characteristic of the stereochemical relationship between the protons. Thus a trans stereochemistry should produce a large coupling constant (~10 Hz), and a cis stereochemistry a small coupling constant (~3 Hz). The product from a stereochemically pure starting material can be characterized precisely as to its stereochemistry by analysis of the NMR spectrum (eq 2). We have prepared the trans

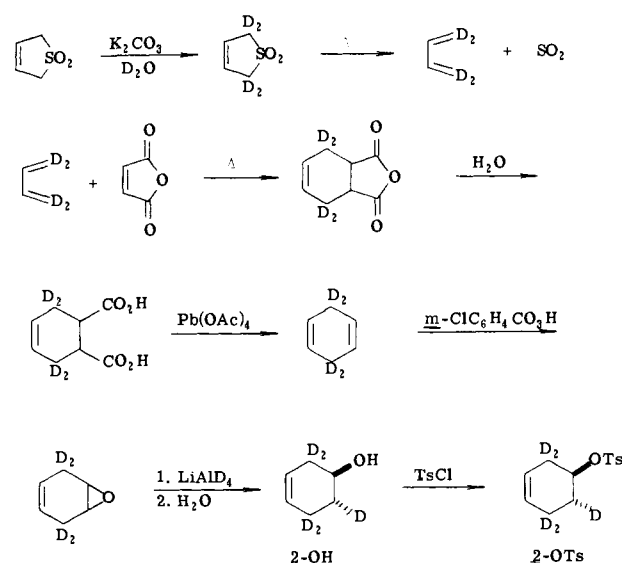


version of cyclohexen-4-yl-3,3,5,6,6-*d*<sub>5</sub> tosylate and carried out solvolytic studies. We report herein the results of these studies, which show the gradation of mechanism within the solvent series aqueous 1,4-dioxane, acetic acid, formic acid, and hexafluoro-2-propanol.<sup>10</sup>

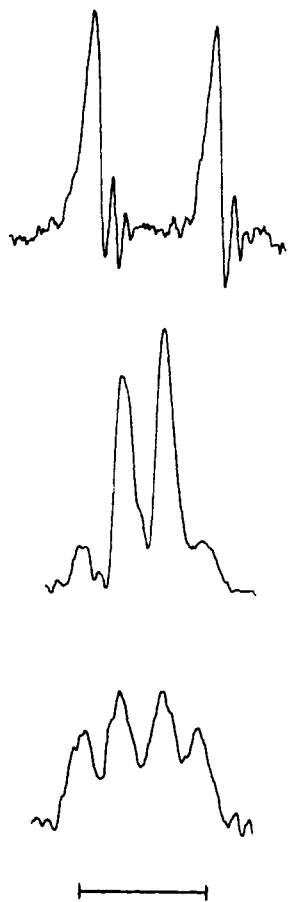
## Results

The synthesis of cyclohexen-4-yl-3,3,5,6,6-*d*<sub>5</sub> tosylate was accomplished by the procedure set out in Scheme I. The

### Scheme I



Diels–Alder reaction of maleic anhydride with butadiene-1,1,4,4-*d*<sub>4</sub>, produced in situ from 2,5-dihydrothiophene-2,2,5,5-*d*<sub>4</sub> 1,1-dioxide, gave an adduct that was hydrolyzed and decarboxylated to cyclohexa-1,4-diene-3,3,6,6-*d*<sub>4</sub>. Monoepoxidation and ring opening with lithium aluminum deuteride



**Figure 1.** (Top) The 4-proton resonance of cyclohexen-4-yl-3,3,5,6,6- $d_5$  tosylate (trans 4,5-H) (2-OTs) with deuterium irradiation ( $J = 9.6$  Hz). (Middle) The 4-proton resonance of cyclohexen-4-yl-3,3,5,6,6- $d_5$  acetate (2-OAc), produced by acetolysis of 2-OTs, with deuterium irradiation. (Bottom) The 4-proton resonance of cyclohexen-4-yl-3,3,5,6,6- $d_5$  formate (2-OF), produced by formolysis of 2-OTs, with deuterium irradiation. The calibration bar represents 10 Hz.

gave cyclohexen-4-yl-3,3,5,6,6- $d_5$  (2-OH), which was transformed into the tosylate (2-OTs) by treatment with tosyl chloride. The proton magnetic resonance spectrum of the 4- and 5-protons of the deuterated tosylate, under conditions of deuterium irradiation, was an AB quartet with  $J = 9.6$  Hz (Figure 1, top, gives half of the quartet). This value of the coupling constant is consistent with the trans relation between the 4- and 5-protons that is expected from the known trans stereochemistry of epoxide ring opening. Although the 4- and 5-protons in the half chair of a cyclohexene are not perfectly antiperiplanar (eq 2), the displacement from the vertical is only about  $11^\circ$ .<sup>11</sup>

Solvolysis was carried out in a series of buffered solvents with a wide range of nucleophilicity and ionizing power (Table I). Kinetics were measured for the solvolysis of 2-OTs in each solvent by following the growth of the tosylate anion methyl resonance and the disappearance of the starting material tosylate methyl resonance. These values are also included in Table I, along with analogous rate constants for the saturated cyclohexyl tosylate. The probe temperature is normally measured to  $\pm 2^\circ\text{C}$ , so the rate constants are not highly accurate. Product studies were carried out on solvolyses that had been allowed to react for 6 half-lives. The product ester, ether, or alcohol was isolated after workup by gas chromatography. The product (2-OS) with the structure corresponding to starting material comprised more than two-thirds of the substitution component in all cases. The approximate product distributions are given in Table II. These VPC figures are not calibrated, but the ac-

**Table II.** Product Distribution (%)<sup>a</sup>

Solvent	5	2-OS	6	Alkenes
Acetic acid	<3	20	10	70 <sup>b</sup>
Formic acid	<3	58	<3	42 <sup>c</sup>
Hexafluoro-2-propanol	10	65	<i>d</i>	25

<sup>a</sup> A quantitative product distribution was not obtained in dioxane/ $\text{H}_2\text{O}$ . <sup>b</sup> 50% 1,4-cyclohexadiene, 20% 1,3-cyclohexadiene plus benzene. <sup>c</sup> 36% 1,4-cyclohexadiene, 6% 1,3-cyclohexadiene. <sup>d</sup> The VPC peak was a small shoulder on that of 2-OS and could not be separated.

etolysis results agree very well with previous studies.<sup>6</sup> Products were stable under the reaction conditions.

The inversion/retention ratio was obtained from the deuterium-irradiated proton spectrum of 2-OS in  $\text{CDCl}_3$ . The 4-proton resonance was a superposition of two nearly isochronous doublets from the retention and inversion products (eq 2). The doublet from the retention product would have the large coupling ( $\sim 10$  Hz) characteristic of the antiperiplanar relationship, whereas the doublet from the inversion product would have the small coupling ( $\sim 3$  Hz) characteristic of the synclinal relationship. Integration of the relative areas of the two doublets gave the retention/inversion ratio (Table III). Figure 1 illustrates the 4-proton resonance for 2-OAc from acetolysis (middle) and for 2-OF from formolysis (bottom). Both doublets are visible, with the retention doublet amounting to about 17% in the acetate and 40% in the formate ( $\pm 2\%$ ). Percentages were calculated from a computer line shape fit and by weighing the peaks. In the hydrolysis only the inversion doublet was observed, and in the hexafluoro-2-propanol only the retention doublet was observed ( $>95\%$ ). Labeling studies were not carried out in trifluoroethanol.

The retention/inversion ratio could also be obtained from the resonances of the 5-proton. Whereas the 4-protons in the retention and inversion products are chemically equivalent and isochronous (save for isotopic differences), the 5-protons are chemically distinct. In the retention product, the 5-proton is axial and in the inversion product it is equatorial. Thus the 5-proton resonances for the two products will differ in chemical shift as well as coupling constant. Figure 2 illustrates the 5-proton resonance for the acetate and the formate. The axial doublet with the large coupling constant is higher field than the equatorial doublet with the small coupling constant. The integration of the 5-proton resonances could be carried out somewhat more cleanly than that of the 4-proton resonances, but the results were essentially identical (Table III). It was fortunate that each product had two NMR spectral regions containing the stereochemical information. The homoallylic product 2-OH from hydrolysis was contaminated to a small extent by the allylic product 6-OH (eq 1), whose resonances obscured the 5-proton resonances from 2-OH. Furthermore, in HFP the 4-proton resonance was obscured by the septet of the methinyl proton from a small amount of contaminating HFP. In acetic and formic acids, full information could be obtained from both spectral regions.

## Discussion

The three general mechanisms we wish to distinguish are solvent displacement ( $k_s$ ) (probably on an ion pair, but we cannot speak to this issue), homoallylic participation ( $k_\Delta$ ), and limiting (localized) carbonium ion ( $k_C$ ). The respective stereochemical consequences of these mechanisms are inversion, retention, and a mixture (racemization in the extreme of symmetrical solvation). We use the term "racemization" loosely in this context to connote equal amounts of inversion and retention. Aqueous dioxane has the highest nucleophilicity

Table III. Stereochemical Analysis

Solvent	$T$ , °C	$t$ , min	$J_{aa}$ , Hz	$J_{ae}$ , Hz	% retention
70% 1,4-dioxane/H <sub>2</sub> O	90	120	$a$	3.4	0
Acetic acid	100	120	9.8	3.3	17
Formic acid	40	225	9.1	3.2	40
Hexafluoro-2-propanol	60	120	10.5	$b$	100

<sup>a</sup> Not observed in the alcohol product; 9.4 Hz measured from synthetic alcohol. <sup>b</sup> Not observed.

and the next to lowest ionizing power (Table I) of the solvents studied. In this solvent, the solvolysis of cyclohexen-4-yl tosylate takes place entirely by displacement with inversion (Table III). This displacement could occur on the neutral tosylate or on an ion pair with positive charge localized at the 4-position.

Acetic acid is more than two orders of magnitude less nucleophilic than aqueous dioxane, but it also is somewhat less ionizing. A retention pathway has just reached the threshold of observation in this solvent (17%, Figures 1 and 2). From this isolated observation, one cannot tell whether the retention pathway results from a  $k_{\Delta}$  or a  $k_C$  mechanism.

Formic acid has about the same nucleophilicity as acetic acid, but is considerably more ionizing (almost four units of  $Y$ ). Thus the retention pathway has reached almost equal importance to the inversion pathway (Figures 1 and 2).

The least nucleophilic and most ionizing solvent by far is hexafluoro-2-propanol. The observation that the inversion pathway has become extinguished and the reaction takes place entirely with retention eliminates the  $k_C$  mechanism as a viable possibility. Thus the mechanism approaches retention, not racemization in solvents of high ionizing power. We therefore conclude that the retention pathway in acetic and formic acids also is a  $k_{\Delta}$ -type mechanism rather than  $k_C$ . This conclusion is in agreement with the results on cyclohexyl tosylate and other secondary systems incapable of a participation pathway,<sup>9</sup> which were found to solvolyze by purely  $k_s$  pathways, rather than  $k_C$ , in acetic and formic acids. HFP also is the only solvent in the present study that produced significant amounts of the rearranged bicyclic product (5) (Table II).

Based entirely on the stereochemical product studies, we can conclude that the solvolysis of cyclohexen-4-yl tosylate changes from a solvent displacement mechanism in highly nucleophilic, poorly ionizing solvents to a participation mechanism in poorly nucleophilic, highly ionizing solvents. There is no evidence for an open, localized carbonium ion.

The kinetics of the reaction indicate that this picture of the mechanism may not be complete (Table I). Rate accelerations usually associated with participation-type mechanisms are absent. The rate is at a maximum in formic acid and is somewhat slower both in aqueous dioxane (high nucleophilicity) and in HFP (high ionizing power). Furthermore, in no solvent is the unsaturated compound significantly more reactive than the saturated system (cyclohexyl tosylate). The rates are reasonably parallel, with an overall rate acceleration by the double bond observed only in formic acid. First, it should be recalled that the double bond is inductively rate retarding, so that anchimeric assistance is larger than the rate ratio indicates in formic acid. Comparisons in HFP and TFE cannot legitimately be made until the hydride shift mechanism (in cyclohexyl) is clarified. The mechanism for cyclohexyl changes from predominately  $k_s$  in formic acid to predominately hydride shift in trifluoroacetic acid,<sup>9</sup> a solvent, like HFP and TFE, of high ionizing power. Until the effect on the rate from this change in mechanism ( $k_s$  to hydride shift) is known, we cannot use cyclohexyl for rate comparisons.

The problem still remains, however, as to the explanation

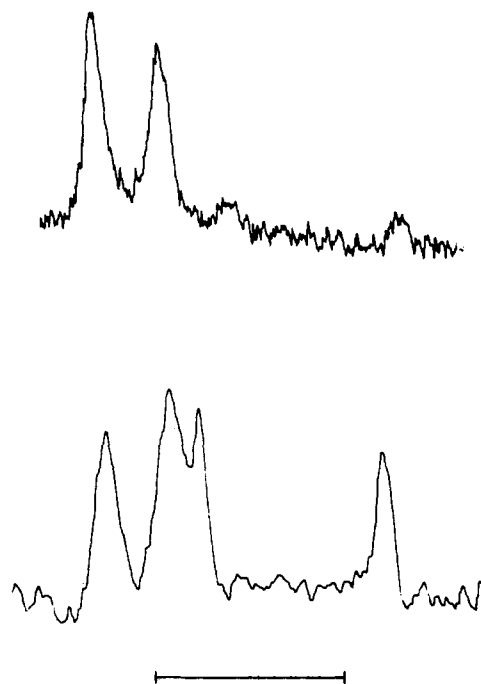


Figure 2. (Top) The 5-proton resonance of cyclohexen-4-yl-3,3,5,6,6- $d_5$  acetate (2-OAc), produced by acetolysis of 2-OTs, with deuterium irradiation. The doublet splittings are 3.3 and 9.8 Hz. (Bottom) The 5-proton resonance of cyclohexen-4-yl-3,3,5,6,6- $d_5$  formate (2-OF), produced by formolysis of 2-OTs, with deuterium irradiation. The calibration bar represents 10 Hz.

for the lack of rate/product correlation for cyclohexen-4-yl tosylate, i.e., increased participation without increased rate. The change in mechanism must be thought of in terms of competing pathways, since neither solvent nucleophilicity nor solvent ionizing power is kept constant. One cannot view the mechanism as an increase in the participation component with the solvent displacement component held constant. If this were the case, one would indeed expect a constantly increasing rate going down the solvent series of Table I. The increase in the participation rate as ionizing power goes up, however, is offset by the decrease in the solvent displacement rate as nucleophilicity goes down. As a result, the maximum rate is observed for formic acid, when both pathways are significant. This view of the reaction is therefore consistent with a true  $k_{\Delta}$  mechanism for the retention pathway, with kinetic participation by double bond in the departure of the leaving group.

A second possibility that is consistent with the product studies is participation by the double bond after rate-determining formation of an ion pair. The details of this mechanism would include ionization without participation, followed either by solvent attack with inversion in solvents of high nucleophilicity or rearrangement to a delocalized homoallylic ion pair that is attacked with retention in solvents of high ionizing power. Thus the stereochemistry is determined after the rate-determining step. Although this explanation is consistent

with the observed stereochemistry, it is not in full agreement with the kinetics. It is unreasonable to expect an approximately constant rate for the initial ionization when the ionizing power is changing by four orders of magnitude (Table I). This mechanistic scenario would have predicted a drastically increasing rate for the solvent series. We therefore favor the first mechanism. In order to maintain an approximately constant rate when two solvent properties (nucleophilicity and ionizing power) are changing rapidly and in opposition, one must invoke two competing mechanisms (solvent displacement and homoallylic assistance), which are respectively favored by one of the solvent properties and whose rates sum up to an approximate constant.

## Conclusions

Cyclohexen-4-yl tosylate solvolyzes by two competitive pathways. The mechanism changes from solvent displacement with complete inversion of configuration in the highly nucleophilic, poorly ionizing solvent aqueous 1,4-dioxane to homoallylic participation with complete retention of configuration in the poorly nucleophilic, highly ionizing solvent hexafluoro-2-propanol. Solvents with intermediate properties exhibit mixtures of the mechanistic pathways (acetic acid, 17% retention; formic acid, 40% retention). The rate passes through a maximum in formic acid, in which both pathways contribute significantly.

## Experimental Section

Routine NMR spectra were recorded on Varian Model T60 and Perkin-Elmer Model R20B spectrometers. Double irradiation of the deuterium resonance was accomplished with a heteronuclear spin decoupler on the R20B. Solvolysis kinetics were measured on the R20B. Analytical and preparative vapor phase chromatography was performed on a Hewlett-Packard Model 700 instrument with a 0.25 in.  $\times$  6 ft column of 10% Carbowax 20 M on Chromosorb W (60/80). Column temperatures were 140 °C (hydrolysis and acetolysis), 130 °C (formolysis), and 115 °C (HFP).

**2,5-Dihydrothiophene-2,2,5,5- $d_4$  1,1-Dioxide.**<sup>12</sup> A solution of 50.0 g of 2,5-dihydrothiophene 1,1-dioxide and 0.5 g of  $K_2CO_3$  in 25 ml of 1,4-dioxane (distilled from  $LiAlH_4$ ) and 60 ml of  $D_2O$  was stirred at room temperature for 48 h. The solvent was removed by rotary evaporation with the flask immersed in dry ice/acetone. The procedure was repeated three times, until deuteration was greater than 98% by NMR. After removal of the solvent by distillation, the product was purified by recrystallization from THF/pentane.

**Diels-Alder Reaction and Hydrolysis.**<sup>13</sup> In a 100-ml round-bottomed flask, equipped with a magnetic stirrer, condenser, and gas trap, were placed 9.0 g of 2,5-dihydrothiophene-2,2,5,5- $d_4$  1,1-dioxide, 6.0 g of maleic anhydride, and 4 ml of xylene. The mixture was stirred and refluxed for 30 min. The solution was cooled, 30 ml of benzene and 1 g of decolorizing carbon were added, and the mixture was warmed on the steam bath for 30 min and filtered. Pentane was added to the filtrate, which was cooled until the anhydride precipitated. The anhydride was dried and then hydrolyzed at elevated temperatures with 100 g of  $H_2O$ . The aqueous solution was cooled, and the diacid (7.5 g, 75%) precipitated, mp 155 °C. The simplified NMR splitting and the disappearance of the upfield resonance indicated that no deuterium scrambling had occurred.

**1,4-Cyclohexadiene-3,3,6,6- $d_4$ .**<sup>14</sup> To 35 ml of previously oxygenated pyridine were added 3.48 g of the diacid and 11.0 g of fresh lead tetraacetate (vacuum dried). As the solution was heated on a steam bath at 50 °C, it became darker and  $CO_2$  evolved. After completion of the

reaction, the mixture was distilled to give 30 ml of pyridine and 1,4-cyclohexadiene. To this mixture 50 ml of  $H_2O$  was added, and the heterogeneous solution was distilled to give 0.5 g (30%) of deuterated diene, NMR (neat)  $\delta$  5.5 (vinyl proton), no resonance at 2.6.

**Cyclohexa-1,4-diene-3,3,6,6- $d_4$  epoxide** was obtained in 40% yield by reaction of 1,4-cyclohexadiene-3,3,6,6- $d_4$  with *m*-chloroperbenzoic acid.

**Cyclohexen-4-yl-3,3,5,6,6- $d_5$  (trans 4,5-H) (2-OH)** was prepared in 50% yield by the reaction of the deuterated cyclohexadiene epoxide with  $LiAlD_4$ .

**Cyclohexen-4-yl-3,3,5,6,6- $d_5$  Tosylate (trans 4,5-H) (2-OTs)** was prepared in 85% yield from the deuterated alcohol by reaction with tosyl chloride; mp 44 °C; NMR ( $CCl_4$ ),  $\delta$  7.5 (half of ABq, 4 H), 5.5 (half of ABq, 2 H), 4.6 (d,  $J = 9.6$  Hz, 1 H), 2.4 (s, 3H), 1.7 (d,  $J = 9.6$  Hz, 1 H). The doublet splitting of 9.6 Hz between the 4- and 5-protons confirmed the trans stereochemistry.

**Solvolyses.** For acetolysis, 0.6 g (0.0023 mol) of the deuterated tosylate was dissolved in 2.7 ml of 0.963 N KOAc in HOAc (1% in  $Ac_2O$ ) to which was added 20.6 ml of HOAc (1% in  $Ac_2O$ ). The reaction was carried out in a sealed ampule, heated in a constant temperature bath for 6 half-lives. Temperatures and times are given in Table III. The solution was cooled, washed with brine, and extracted with five 50-ml portions of ethyl ether. The organics were neutralized ( $NaHCO_3$  solution) and dried ( $MgSO_4$ ). The ether was removed by careful distillation, and the products were analyzed by vapor phase chromatography. The products were found to be stable under the reaction conditions. The formolysis was carried out in the same fashion with 25 ml of formic acid that had been distilled from boric anhydride. For the hexafluoro-2-propanolysis, 0.6 g of the tosylate was dissolved in 2 ml of HFP containing 0.3 g of pyridine as buffer. After the reaction, the solution was washed with  $H_2O$ , dried ( $MgSO_4$ ), and analyzed directly by VPC. For the hydrolysis, 0.6 g of the tosylate was dissolved in 17.5 ml of 1,4-dioxane and 7.5 ml of  $H_2O$ , containing 0.46 g (0.0046 mol) of 2,6-lutidine. The reaction product was poured into excess  $H_2O$  and extracted with ethyl ether. The organics were washed with ice-cold 10% HCl, saturated  $NaHCO_3$ , and saturated NaCl. The dried ( $K_2CO_3$ ) solution was concentrated and analyzed by VPC.

**Kinetics** were obtained by following the growth of the methyl resonance of the tosylate anion and the decrease in the methyl resonance of the starting tosylate as a function of time. Errors are expected to be high ( $\sim 15\%$ ).

## References and Notes

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