

0.5 mL of SO<sub>2</sub> was slowly added a clear, homogeneous solution of magic acid (1 mL) in SO<sub>2</sub> (ca. 1 mL) at dry ice-acetone temperature with efficient vortex mixing. A cold aliquot was withdrawn with a precooled pipet (SO<sub>2</sub>) and transferred into a 5-mm NMR tube under nitrogen, to which ca. 5 drops of cold CD<sub>2</sub>Cl<sub>2</sub> had been added (vortex). NMR spectra were recorded at -65 °C.

**Molecular Modeling.** MMX force field energy calculations on the sulfoxide substrates were carried out by using the PCMODEL program (Serene Software). Good convergence was achieved after

100 iterations. The CSC angles were obtained directly from the minimized structures.

**Acknowledgment.** We are most grateful to Professor George Olah for his interest in our work and valuable suggestions on this manuscript. We thank KSU for research support and the Ohio Academic Challenge Program for the funds for a high-field NMR spectrometer.

## Solvolysis Rates and $\beta$ -Deuterium Secondary Kinetic Isotope Effects of Some Tertiary and Secondary Alk-5-enyl Derivatives. Evidence for $\pi$ -Participation

Mirko Orlović, Stanko Borčić,\* Krešimir Humski, Olga Kronja, Vera Imper, and Eugenio Polla

Faculty of Pharmacy and Biochemistry, University of Zagreb, A. Kovačića 1, 41000 Zagreb, Yugoslavia

Veron J. Shiner, Jr.

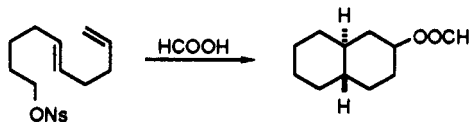
Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Received March 27, 1990

Tertiary 1,1-dimethylalk-5-enyl chlorides solvolyze in 80% v/v ethanol with no or moderate rate enhancements attributable to  $\pi$ -participation. However, secondary  $\beta$ -deuterium kinetic isotope effects (KIE, two deuterated methyl groups) are significantly reduced ( $k_H/k_D = 1.22$ – $1.57$ ) relative to the saturated analogues ( $k_H/k_D = 1.80$ ), indicating participation of the double bond. Secondary 1-methylalk-5-enyl tosylates show the same trends, i.e., no or very moderate rate enhancements but reduced  $\beta$ -deuterium secondary KIE relative to the saturated analogue.

### Introduction

Biomimetic cationic polycyclizations have been extensively investigated.<sup>1,2</sup> A great deal of fascinating synthetic work has been reported. It was demonstrated that (poly)cyclic products are obtained from mono-, di-, and polyolefinic substrates with a variety of leaving groups in reactions that proceed by way of carbocation intermediates; under appropriate conditions rings may be produced with high stereoselectivity or stereospecificity from epoxides, acetals, or sulfonate esters. For example, the formolysis of 5,9-decadienyl *p*-nitrobenzenesulfonate proceeds with bicyclization to yield decalin products stereospecifically.<sup>3</sup> From the *E* isomer only the *trans*-decalin ester is formed while the *Z* isomer gives exclusively the *cis*-decalin derivative.



The cyclization mechanism is, however, not well understood; it is not certain whether the final product arises by way of formation of an initial carbenium ion intermediate, which then cyclizes in a stepwise manner through discrete partially cyclized intermediates, whether only the

formation of the first ring is concerted with the departure of the leaving group, or whether the whole polycyclization process is concerted. Concerted processes inevitably involve  $\pi$ -participation, i.e., one or more double bonds would be involved in the rate-determining formation of the carbocation. The usual method for detecting such participation involves the comparison of reaction rates. Unfortunately, kinetic data reported in the literature are scarce. We therefore initiated an investigation involving measurements of solvolysis rates of pertinent substrates. As a first step, we set out to detect simple  $\pi$ -participation, i.e., to investigate the reactivity of olefinic substrates containing only one CC double bond at the 5-position.<sup>4,5</sup>

For biomimetic cationic monocyclization, the reported rate data are not without ambiguity. Bartlett<sup>6</sup> and Trahanovsky<sup>7</sup> demonstrated that the solvolysis of 5-hexenyl *p*-nitrobenzenesulfonate proceeds with a slight rate enhancement relative to the saturated analogue and produces some cyclohexyl and methylcyclopentyl derivatives. Van Tamelen<sup>8</sup> reported that the acid-catalyzed epoxide ring opening of 1 proceeds with extensive cyclization and at a rate much faster than that of its saturated analogue. In our previous work we extensively examined solvolysis rates of a series of benzylic chlorides 2 and their saturated analogues.<sup>9</sup> Although the observed rate enhancements due

(1) For preliminary communication, see: Orlović, M.; Humski, K.; Borčić, S.; Polla, E. *J. Chem. Soc., Chem. Commun.* 1986, 263.

(2) For reviews, see: (a) Dugs, H.; Penney, C. *Bioorganic Chemistry*; Springer-Verlag: New York, 1981; pp 318–328. (b) Johnson, W. S. *Bioorg. Chem.* 1976, 5, 51. (c) Van Tamelen, E. E. *Acc. Chem. Res.* 1975, 8, 152.

(3) (a) Johnson, W. S.; Bailey, D. M.; Owyang, R.; Bell, R. A.; Jaques, B.; Crandall, J. K. *J. Am. Chem. Soc.* 1964, 86, 1959. (b) Johnson, W. S.; Crandall, J. K. *J. Org. Chem.* 1965, 30, 1785.

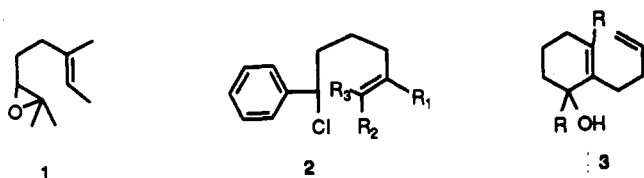
(4) For evidence of extended  $\pi$ -participation, see: (a) Kronja, O.; Polla, E.; Borčić, S. *J. Chem. Soc., Chem. Commun.* 1982, 1044. (b) Ho, N.; Le Noble, W. J. *J. Org. Chem.* 1989, 54, 2018.

(5) A case of stepwise polycyclizations has been reported: Nishisawa, M.; Takenaka, H.; Hayashi, Y. *J. Am. Chem. Soc.* 1985, 107, 522.

(6) (a) Bartlett, P. D.; Closson, W. D.; Cogdell, T. J. *J. Am. Chem. Soc.* 1965, 87, 1308. (b) Bartlett, P. D. *Justus Liebig's Ann. Chem.* 1967, 89, 4867.

(7) Trahanovsky, W. S.; Doyle, M. P. *J. Am. Chem. Soc.* 1967, 89, 4867.

(8) Van Tamelen, E. E.; James, D. R. *J. Am. Chem. Soc.* 1977, 99, 950.



to the presence of the aliphatic double bond were relatively small, it was demonstrated (by  $\rho\sigma$  correlations,  $\alpha$ -,  $\beta$ -,  $\omega$ -deuterium secondary kinetic isotope effects, methyl substituent rate effects, and activation parameters) that most of these chlorides react with neighboring group assistance. On the other hand, Sunko<sup>10</sup> could find no evidence for participation in formolysis of 3.

For participating systems, the experimentally measured solvolysis rate constant  $k_{\text{exp}}$  (often titrimetric) can in the first approximation be considered to be the sum of the rate constants for the unassisted process ( $k_c$ ) and the neighboring group assisted process ( $k_\Delta$ ).

$$k_{\text{exp}} = k_c + k_\Delta$$

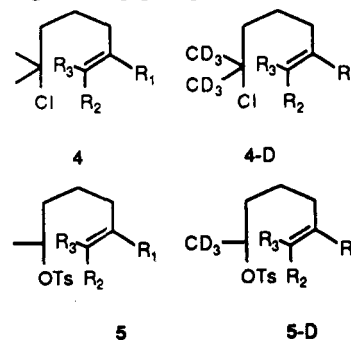
The fraction of products arising by way of participation is then given by  $k_\Delta/(k_c + k_\Delta)$ . Since  $k_c$  cannot be measured directly, it is approximated from the solvolysis rate of a reference compound of similar structure which lacks the neighboring group. Because of this approximation, only large rate enhancements ( $k_\Delta \gg k_c$ ) can be considered as a valid proof of participation. Small rate effects due to the presence of the neighboring group are ambiguous *but do not prove the lack of participation*. If  $k_\Delta \approx k_c$ , the uncertainty of the  $k_c$  value used can affect considerably the calculation of the  $k_\Delta$  value and even conceal important participation. If the reaction involves a two-step mechanism with an intermediate ion pair, then participation may compete at the ion-pair stage with the normal reaction of solvent separation or solvent nucleophilic attack. If the proportion of internal return is small, the above analysis does not apply and capture by participation at the ion-pair stage might not involve much rate acceleration.

Many of these ambiguities can be avoided by the measurement of  $\beta$ -deuterium secondary kinetic isotope effects (KIE). Substrates deuterated at the  $\beta$ -position relative to the point of attachment of the leaving group show a rate depression relative to the protio analogue in solvolysis. This effect is relatively large in limiting solvolyses if it is due to a deuterated methyl group attached to the reaction center. The cause of this KIE has been shown to be hyperconjugative electron release from the neighboring C-H(D) bond to the incipient empty p orbital in the transition state. If neighboring group participation is operative, then the orbital vacancy is, in part at least, delocalized away from the reaction center; less hyperconjugative interaction occurs, resulting in a lower  $\beta$ -deuterium KIE.<sup>1</sup> This method has been shown to be more reliable and more sensitive for detecting participation than simple rate ratios especially in cases when the observed rate enhancements are small.

Finally it should be mentioned that theory seems to favor concerted monocyclizations relative to the stepwise reaction. Concerted reactions can be considered as laticyclic processes; Goldstein and Hoffmann<sup>11</sup> have shown that [0 + 2] interactions present in a concerted monocyclization would stabilize a (nonclassical) carbonium ion

like transition state. Dewar,<sup>12</sup> on the basis of MINDO/3 calculations, considers a  $\pi$ -complex (formed from the incipient empty p orbital and the  $\pi$ -electrons of double bond) as the most stable structure for the transition state.

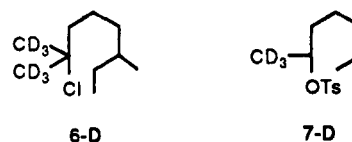
The research reported herein deals with solvolytic reactivity of tertiary (4, 4-D) and secondary (5, 5-D) alk-5-enyl chlorides and tosylates, respectively. The rates of 4 and 5 ( $k_u$ ) are compared to those of their saturated analogues ( $k_s$ ).  $\beta$ -Deuterium secondary KIEs were measured ( $k_H/k_D$ , 4 vs 4-D and 5 vs 5-D) and their magnitudes compared to those obtained with analogous compounds lacking the neighboring group.



- a  $R_1 = R_2 = R_3 = H$
- b  $R_1 = R_3 = H, R_2 = CH_3$
- c  $R_1 = R_2 = H, R_3 = CH_3$
- d  $R_1 = CH_3, R_2 = R_3 = H$
- e  $R_1 = R_2 = CH_3, R_3 = H$

## Results

The series of tertiary alk-5-enyl chlorides (4, 4-D) were prepared by the reaction of parent alcohols with thionyl chloride. The parent alcohols were prepared by reaction of the required alkenyllithium derivatives with either acetone or deuterioacetone. The series of secondary alk-5-enyl tosylates (5, 5-D) were prepared from the corresponding alcohols in the usual way (TsCl and pyridine). Parent alcohols were obtained from Grignard reagents (RMgBr) and either acetaldehyde or 2,2,2-trideuterioacetaldehyde. In the same way the saturated analogues 6-D and 7-D were prepared in order to compare their  $\beta$ -deuterium secondary KIEs with those measured for the unsaturated analogues 4-D and 5-D, respectively. Details are given in the Experimental Section.



The chlorides and tosylates were subjected to solvolysis in 80% v/v ethanol-water (80E) and/or 97% w/w 2,2,2-trifluoroethanol-water (97T), and the reaction rates were followed by automatic pH-state titration of the liberated acid. Typically, 0.05 mmol of the substrate was dissolved in 20 mL of the solvent thermostated to  $\pm 0.1$  °C, and the liberated acid was titrated with 0.008 M sodium hydroxide in the same solvent mixture. Each measurement was carried out at least three times and for KIE determinations five to six times. In all cases the reactions were first order to at least 90% reaction. First-order rate constants were calculated from about 100 determinations made between 15 and 80% reaction, using a nonlinear least-squares program. Activation parameters were calculated from rate

(9) (a) Polla, E.; Borčić, S.; Sunko, D. E. *J. Org. Chem.* 1979, 44, 4098.  
 (b) Mihel, L.; Orlović, M.; Polla, E.; Borčić, S. *J. Org. Chem.* 1979, 44, 4086.  
 (c) Polla, E.; Borčić, S.; Sunko, D. E. *Tetrahedron Lett.* 1975, 799.

(10) Ladika, M.; Bregovec, I.; Sunko, D. E. *J. Am. Chem. Soc.* 1981, 103, 1286.

(11) Goldstein, M. J.; Hoffmann, R. *J. Am. Chem. Soc.* 1971, 93, 6193.

(12) Dewar, M. J. S.; Reynolds, C. H. *J. Am. Chem. Soc.* 1984, 106, 1744.

**Table I. Solvolysis Rate Constants and Activation Parameters of Some 1,1-Dimethylalk-5-enyl Chlorides in 80% v/v Ethanol**

| (CH <sub>3</sub> ) <sub>2</sub> C(Cl)R |                     | temp, °C | 10 <sup>5</sup> <i>k</i> , s <sup>-1</sup> | Δ <i>H</i> <sup>‡</sup> , <sup>c</sup> kJ mol <sup>-1</sup> | Δ <i>S</i> <sup>‡</sup> , <sup>c</sup> J K <sup>-1</sup> mol <sup>-1</sup> |
|--|---------------------|----------|--|---|--|
| R                                      | compd <sup>a</sup>  |          |  |   |  |
|  | 4a <sup>17-19</sup> | 60       | 56.8 (1)                                   | 88.7 ± 4.1  | 41.5 ± 12.9  |
|  |                     | 50       | 21.0 (5)                                   |   |  |
|  |                     | 40       | 6.94 (3)                                   |   |  |
|  | 4b                  | 60       | 85.1 (1)                                   | 92.0 ± 2.1  | 28.4 ± 6.5   |
|  |                     | 50       | 29.0 (5)                                   |   |  |
|  |                     | 40       | 9.7 (2)                                    |   |  |
|  | 4c                  | 60       | 56.9 (1)                                   | 93.4 ± 6.2  | 27.6 ± 19.0  |
|  |                     | 50       | 19.4 (4)                                   |   |  |
|  |                     | 40       | 5.96 (5)                                   |   |  |
|  | 4d <sup>20</sup>    | 60       | 109 (1)                                    | 94.3 ± 2.4  | 19.4 ± 7.5   |
|  |                     | 50       | 37.9 (1)                                   |   |  |
|  |                     | 40       | 11.8 (1)                                   |   |  |
|  | 4e <sup>21</sup>    | 60       | 841 (3)                                    | 86.2 ± 2.0  | 28.9 ± 6.2   |
|  |                     | 50       | 330 (1)                                    |   |  |
|  |                     | 40       | 146 (2)                                    |   |  |

<sup>a</sup>Preparation described in references. <sup>b</sup>The uncertainty of the last reported figure (standard deviation of the mean) is shown in parentheses. <sup>c</sup>Uncertainties are standard deviations.

**Table II. Relative Solvolysis Rates and β-Deuterium Secondary Kinetic Isotope Effects of Some 1,1-Dimethylalk-5-enyl and 1,1-Dimethylalkyl Chlorides in 80% v/v Aqueous Ethanol at 50 °C**

| (CD <sub>3</sub> ) <sub>2</sub> C(Cl)R |       | <i>k<sub>u</sub></i> / <i>k<sub>s</sub></i> <sup>a</sup> | <i>k<sub>H</sub></i> / <i>k<sub>D</sub></i> <sup>b</sup> |
|--|-------|--|--|
| R                                      | compd |  |  |
|  | 6-D   |  | 1.79 (3) <sup>c</sup>                                    |
|  |       |  | 1.80 (3)   |
|  | 4a-D  | 0.78   | 1.57 (2)   |
|  |       |  |  |
|  | 4b-D  | 1.25   | 1.38 (1)   |
|  |       |  |  |
|  | 4c-D  | 0.75   | 1.72 (4)   |
|  |       |  |  |
|  | 4d-D  | 1.63   | 1.22 (3)   |
|  |       |  |  |
|  | 4e-D  | 18.9   | 1.37 (3)   |
|  |       |  |  |

<sup>a</sup>*k<sub>u</sub>* is the rate of the alk-5-enyl chloride. *k<sub>s</sub>* is the rate of the corresponding alkyl chloride. *k<sub>s</sub>* values are given in ref 11. Ratios are for protio compounds. <sup>b</sup>For six deuterium atoms. The uncertainty of the last reported figure (standard deviation of the mean) is shown in parentheses. <sup>c</sup>At 25 °C, ref 13.

data determined at three different temperatures.

Solvolysis rate constants and activation parameters for 4 are given in Table I while the relative rates (*k<sub>u</sub>*/*k<sub>s</sub>*) and β-deuterium secondary KIE (4 vs 4-D) are given in Table II.

Kinetic data for solvolysis of secondary alk-5-enyl tosylates 5 and the some related alkyl derivatives<sup>13</sup> are given in Table III. Relative rates and some relevant β-deuterium secondary KIE are reported in Table IV.

### Experimental Section

Deuterium content of deuterated compounds was determined by <sup>1</sup>H NMR spectroscopy and was found to be over 95% of the theory in all cases.

**Alk-4-enyl Bromides.** Alk-4-enyl alcohol (0.1 mol) and pyridine (0.043 mol) were dissolved in 50 mL of petroleum ether, and the solution was cooled and maintained at 0 °C. The solution of PBr<sub>3</sub> (0.043 mol) in 20 mL of petroleum ether was added dropwise to the stirred solution. Stirring and cooling were con-

tinued for an hour. Then, a few milliliters of cold water were added into the reaction mixture. The water layer was removed, into the residue ether was added, and the solution was washed with water and dried over anhydrous CaCl<sub>2</sub>. The solution was filtered, the solvent evaporated, and the crude bromide distilled under reduced pressure. The yields of obtained products that gave expected <sup>1</sup>H NMR spectra were 45–50%.

**1,1-Dimethylalk-5-enyl Alcohols and Their Deuterated Analogues.** Granulated lithium was placed in 20 mL of anhydrous ether. Alk-5-enyl bromide (0.01 mol) and acetone or acetone-*d*<sub>6</sub> (0.01 mol) were dissolved in 10 mL of anhydrous ether and added dropwise onto the lithium at such a rate as to maintain the reaction mixture refluxing. (If the reaction did not start, the mixture was slightly heated.) Then, the mixture was refluxed for an hour. Lithium was removed and a new portion of 20 mL of ether was poured into the reaction mixture. The solution was washed twice with water and dried over anhydrous MgSO<sub>4</sub>. Ether was evaporated and the crude alcohol distilled under reduced pressure. The yields of obtained products that gave expected <sup>1</sup>H NMR spectra was 55–73%.

New (protio) parent alcohols of corresponding chlorides in parentheses are 4b and 4c.

(*E*)-2-Methyl-6-octen-2-ol (4b). Anal. Calcd for C<sub>9</sub>H<sub>18</sub>O: C, 76.00; H, 12.75. Found: C, 75.84; H, 12.91.

(*Z*)-2-Methyl-6-octen-2-ol (4c). Anal. Calcd for C<sub>9</sub>H<sub>18</sub>O: C, 76.00; H, 12.75. Found: C, 75.99; H, 12.86.

**1-Methylalk-5-enyl Alcohols and Their Deuterated Analogues.** Magnesium (0.02 mol) and a crystal of iodine were placed in a round-bottom three-necked flask and heated until the iodine covered the surface of magnesium. Then, 10 mL of anhydrous ether was poured onto the magnesium and 2–3 drops of alk-4-enyl bromide was added. The mixture was heated until the color caused by iodine disappeared. Alk-4-enyl bromide (0.02 mol) was dissolved in 15 mL of anhydrous ether and added dropwise in the stirred reaction mixture at such a rate as to maintain the mixture refluxing. Then the reaction mixture was refluxed and stirred for an hour. The obtained Grignard reagent was cooled to 0 °C, and the solution of acetaldehyde or acetaldehyde-*d*<sub>8</sub> (0.02 mol) in 20 mL of anhydrous ether was added dropwise. The mixture was then stirred at room temperature for 2 h. When the reaction was completed (checked with TLC) the Grignard complex was destroyed with a saturated solution of NH<sub>4</sub>Cl. The formed precipitate was removed by filtration, the layers were separated, and the water layer washed with ether three times. The combined ether solutions were washed with 3% solution of Na<sub>2</sub>CO<sub>3</sub> and dried over MgSO<sub>4</sub>. The solution was then filtered, the ether evaporated, and the crude alcohol distilled under reduced pressure. The obtained products gave the expected <sup>1</sup>H NMR spectra and the yields were 43–57%.

New (protio) parent alcohols of corresponding tosylates in parentheses are 5c and 5e.

(*Z*)-6-Octen-2-ol (5c). Anal. Calcd for C<sub>8</sub>H<sub>16</sub>O: C, 74.82; H, 12.71. Found: C, 75.04; H, 12.59.

(13) Rate constants of several saturated derivatives were reported previously, see: Orlović, M.; Kronja, O.; Humski, K.; Borčić, S. *J. Org. Chem.* 1986, 51, 2925.

Table III. Solvolysis Rates and Activation Parameters of Some 1-Methylalk-5-enyl and 1-Methylalkyl Tosylates

| CH <sub>3</sub> CH(OTs)R |                        | 10 <sup>6</sup> k, s <sup>-1</sup> at T, °C <sup>c</sup> |          |          |            | $\Delta H^\ddagger$ , <sup>d</sup> kJ mol <sup>-1</sup> | $\Delta S^\ddagger$ , <sup>d</sup> J K <sup>-1</sup> mol <sup>-1</sup> |
|--------------------------|------------------------|--|----------|----------|------------|---|--|
| R                        | compd <sup>a</sup>     | solvent <sup>b</sup>                                     | 70       | 60       | 50         |   |  |
|                          | 7                      | 97T  | 28.9 (3) | 10.7 (1) | 3.21 (1)   | 97.6 ± 2.4  | 28.9 ± 7.3   |
|                          | 5a                     | 80E  | 34.8 (1) | 15.6 (2) | 5.14 (2)   | 85.4 ± 6.9  | 62.6 ± 20.5  |
|                          |                        | 97T  | 26.6 (3) | 10.1 (2) | 4.29 (2)   | 81.0 ± 4.3  | 78.4 ± 12.9  |
|                          | 5b <sup>22</sup>       | 97T  | 26.5 (3) | 10.7 (1) | 3.33 (2)   | 97.6 ± 2.4  | 28.9 ± 4.8   |
|                          |                        | 80E  | 25.7 (3) | 10.8 (2) | 3.00 (3)   | 96.3 ± 9.2  | 33.3 ± 27.9  |
|                          | 97T                    | 32.8 (1)   | 13.8 (3) | 4.57 (2) | 82.8 ± 4.5 | 63.4 ± 13.9   |  |
|                          | 5c                     | 80E  | 33.8 (1) | 12.2 (3) | 4.38 (8)   | 91.2 ± 1.5  | 46.2 ± 4.4   |
|                          |                        | 97T  | 47.8 (5) | 24.2 (7) | 6.51 (1)   | 89.0 ± 5.2  | 48.2 ± 43.6  |
|                          | 97T                    | 20.0 (2)   | 7.64 (2) | 3.91 (5) | 67.9 ± 8.5 | 113.1 ± 26.4  |  |
|                          | 5d <sup>17,23,24</sup> | 80E  | 38.8 (1) | 15.9 (2) | 5.48 (6)   | 87.4 ± 3.1  | 56.1 ± 9.2   |
|                          |                        | 97T  | 211 (3)  | 88.7 (7) | 33.7 (4)   | 81.7 ± 1.2  | 58.7 ± 3.7   |
|                          | 5e <sup>21</sup>       | 80E  | 40.3 (3) | 16.0 (2) | 6.55 (8)   | 80.8 ± 2.2  | 75.2 ± 6.7   |
|                          |                        | 97T  | 211 (3)  | 88.7 (7) | 33.7 (4)   | 81.7 ± 1.2  | 58.7 ± 3.7   |

<sup>a</sup>Preparation described in references. <sup>b</sup>80E is 80% v/v aqueous ethanol, 97T is 97% w/w aqueous 2,2,2-trifluoroethanol. <sup>c</sup>The uncertainty of the last reported figure (standard deviation of the mean) is shown in parentheses. <sup>d</sup>The uncertainty is standard deviation.

Table IV. Relative Solvolysis Rates and  $\beta$ -Deuterium Secondary Kinetic Isotope Effects of Some 1-Methylalk-5-enyl Tosylates at 50 °C

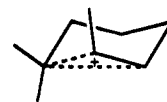
| (CD <sub>3</sub> CH(OTs)R |       | solvent <sup>a</sup> | $k_u/k_s$ <sup>b</sup> | $k_H/k_D$ <sup>c</sup> |
|---------------------------|-------|----------------------|------------------------|------------------------|
| R                         | compd |                      |                        |                        |
|                           | 7     | 80E                  |                        | 1.47 (5)               |
|                           |       | 97T                  |                        | 1.37 (6)               |
|                           | 5a    | 80E                  | 0.87                   |                        |
|                           |       | 97T                  | 1.34                   |                        |
|                           | 5c    | 80E                  | 0.59                   |                        |
|                           |       | 97T                  | 1.37                   |                        |
|                           | 5d    | 97T                  | 1.17 <sup>d</sup>      | 1.20 (5)               |
|                           | 5e    | 80E                  | 1.20                   | 1.13 (2)               |
|                           |       | 97T                  | 10.1 <sup>d</sup>      | 1.16 (2)               |

<sup>a</sup>80E is 80% v/v aqueous ethanol. 97T is 97% w/w 2,2,2-trifluoroethanol. <sup>b</sup> $k_u$  is the rate constant for the alk-5-enyl and  $k_s$  for that of the corresponding alkyl tosylate.  $k_s$  values not given in Table III are reported in ref 11. <sup>c</sup>The uncertainty of the last reported figure (standard deviation of the mean) is shown in parentheses. <sup>d</sup>Relative to  $k_s$  of 2-heptyl tosylate under the assumption that as with 80E,  $k_s$  is not dependent upon the number of C atoms and branching in R also in 97T. Thus 2-hexyl (7) and 2-heptyl tosylate solvolyze in 97T at practically the same rate (Table III).

(*E*)-6-Methyl-6-octen-2-ol (5e). Anal. Calcd for C<sub>9</sub>H<sub>18</sub>O: C, 76.00; H, 12.75. Found: C, 76.18; H, 12.71.

**1,1-Dimethyl-5-alkenyl Chlorides and Their Deuterated Analogues.** Tertiary alcohol (1 mmol) was dissolved in 3 mL of methylene chloride, and the solution cooled to -20 °C. The pressure over the solution was lowered to 100 Torr and thionyl chloride (0.05 mL) was added. After half an hour, the temperature was raised to 0 °C and the second portion of thionyl chloride (0.05 mL) was poured into the reaction mixture. The stirring was continued for 1 h, and then the solvent was evaporated. The yields of crude products were 70–90% and were used for kinetic measurements.

**1-Methylalk-5-enyl Tosylates and Their Deuterated Analogues.** Secondary alcohol (10 mmol) was dissolved in 50 mL of anhydrous pyridine, tosyl chloride (10.5 mmol) was dissolved in 10 mL of anhydrous pyridine, and the solutions were cooled to -20 °C and then joined. The solution was kept for 3 days at 0 °C and during this period crystals of pyridinium hydrochloride were formed. The reaction mixture was then poured into 15–20 mL of cooled water (0 °C) and the product extracted three times with ether. The combined ether solutions were washed with 1 M HCl and 3% Na<sub>2</sub>CO<sub>3</sub> and dried over anhydrous MgSO<sub>4</sub>. The solvent was evaporated, and the crude products, which gave expected <sup>1</sup>H NMR spectra, were used for kinetic measurements. The yields were 80–95%.

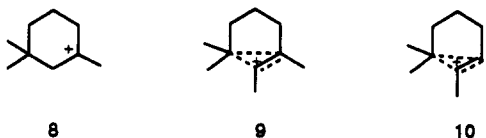


Even with 4a, the chloride with only a single alkyl substituent on the double bond, a significantly reduced KIE is observed, although the rate effect ( $k_u/k_s$ ) is inverse. This can be taken as an indication that at least a part of the reaction proceeds by way of  $k_A$ . The driving force for this reaction is the transformation of a  $\pi$  to a  $\sigma$  bond, which compensates for the unfavorable conversion of a tertiary to a secondary carbocation.



Curiously, the smallest KIE is observed with the chloride 4d and not with 4e, which is the only one to show a rate enhancement. We rationalize this observation by consideration of the distribution of the charge in the reaction transition state. In the former case the transition state

is more akin to the tertiary cyclohexyl cation **8** with relatively less charge at the reaction center, i.e., a "late" transition state.



In the latter case the transition state occurs earlier and is more like the carbonium ion **9** in which three tertiary centers compete to accommodate the incipient positive charge. With **4b** the closure of the ring is relatively unfavorable since it would place the positive charge on a secondary carbon; perhaps only a portion of the reaction proceeds by  $\pi$ -participation (carbonium ion **10**).

There is good reason to believe that tertiary alkyl chlorides solvolyze by rate-determining dissociation of the reversibly formed intimate ion pair and that  $k_H/k_{\beta-d_3}$  isotope effects around 1.80 pertain to the ion-pair separation step as being rate determining. This effect of 1.80 or 1.34 per  $CD_3$  group for the tertiary example compares with  $\sim 1.46$  per  $CD_3$  group for secondary sulfonate esters in the same (solvent separation) rate-determining step. Larger demand from the secondary cationic center leads to the larger  $\beta$ -d effect. With the secondary esters the isotope rate effect per  $CD_3$  group for the ionization step has been established as  $\sim 1.20$  or about the square root of the effect when solvent separation is rate determining. By analogy, one might expect the effect per  $CD_3$  group for rate-determining ionization of the tertiary chloride to be around 1.16 or about 1.34 for two  $CD_3$  groups.  $\pi$ -Participation of the type being considered here could take place in the ionization step itself or at the ion-pair stage; in the latter case perhaps even by a preassociation-type mechanism in which  $\pi$ -nucleophilic attack would compete with solvent separation for carbonium ion capture. Thus  $\beta$ - $d_3$  isotope effects lower than 1.80 but higher than 1.34 might arise by  $\pi$ -participation occurring either during ionization or after reversible or partly reversible ionization; effects around 1.34 might be due to rapid capture after rate-determining ionization but effects lower than 1.34 could be either due to participation during ionization or, if capture is reversible (which seems unlikely), some subsequent step.

It is to be noted that there is no correlation between the rate effects ( $k_u/k_s$ ) and KIE ( $k_H/k_D$ ). Thus these two parameters are different indicators of the transformation occurring in the reaction rate-determining step.

**Secondary Alk-5-enyl Tosylates.** At first sight the trends in solvolysis rates of the title compounds (Tables III and IV) seem to parallel those with the tertiary chlorides and one is tempted to draw the same conclusions. Again, there are no significant rate effects ( $k_u/k_s$ ) except possibly with the substrate having a trisubstituted double bond in 97T (**5e**). KIEs for unsaturated tosylates **5d** and **5e** are significantly lower than those of the saturated analogue **7**. However, one problem here lies with the KIE for the reference saturated tosylate **7**. Secondary alkyl derivatives solvolyze, unlike the tertiary chlorides, with a secondary  $\beta$ -deuterium KIE whose magnitude depends on the particular combination of several possible rate-deter-

mining steps, which in turn may depend on the nature of the alkyl group. Thus isopropyl brosylate with one  $CD_3$  group reacts in 90E with a KIE of only 1.13 (25 °C), 1.19 in 50E, and 1.21 in 97T.<sup>14</sup> The analogous KIE with 3-pentyl brosylate with one deuterated methylene group in 70E is 1.31.<sup>15</sup> These "borderline" solvolyses have several energetically nearly equivalent reaction paths a their disposal. Thus small changes in reaction conditions (solvent, temperature, and structure of the alkyl groups) can change the reaction mechanism.

For rate-determining unassisted ionization the KIE for one  $\alpha$ - $CD_3$  group has been determined to be  $\sim 1.20$  while for rate-determining ion-pair separation it is  $\sim 1.46$ , for rate-determining attack by solvent oxygen nucleophile on the ion pair it is  $\sim 1.20$ , and for rate-determining proton elimination from the deuterated methyl group it is between 2.5 and 3.0.

The  $\beta$ - $d_3$  effects for the saturated reference reactant, **7**, are at or near the maximum expected for rate-determining ion-pair separation; the KIE caused by  $\alpha$ -deuterium substitution in **7** has also been measured and found to be 1.22 in both 80E and 97T, also consistent with rate-determining ion-pair separation. The smaller  $\beta$ - $d_3$  effects found for **5d** (1.20) are consistent with a mechanism that involves rate-determining ionization or rate-determining capture by the  $\pi$ -bond electrons after reversible ionization; since the rate is not accelerated by the neighboring group, the latter possibility seems most likely and could occur by a preassociation mechanism in which capture by the  $\pi$  bond replaces the rate-determining solvent separation process of the unsaturated analogue. Compound **5e**, which shows  $\beta$ - $d_3$  isotope effects of 1.13 (80E) and 1.16 (97T) along with some acceleration (10 $\times$ ) in the latter solvent, apparently ionizes with participation.

**Acknowledgment.** This research has been partly financed by the American-Yugoslav Board for Scientific and Technological Cooperation. (Research Council of Croatia and NSF.)

**Supplementary Material Available:** <sup>1</sup>H NMR spectra for corresponding carbinols of **4b**, **4b-D**, **4c**, **4c-D**, **5c**, **5e**, and **5e-D** (4 pages). Ordering information is given on any current masthead page.

(14) Shiner, V. J., Jr.; Fisher, R. D.; Dowd, W. *J. Am. Chem. Soc.* **1969**, *91*, 7748.

(15) Shiner, V. J., Jr. In *Isotope Effects in Chemical Reactions*; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand Reinhold Company; New York; p 129.

(16) Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1953**, *75*, 2925.

(17) Ashby, E. C.; Oswald, J. *J. Org. Chem.* **1988**, *53*, 6068.

(18) Lustyuk, J.; Maillard, B.; Deycard, S.; Lindsay, D. A. *J. Org. Chem.* **1987**, *52*, 3509.

(19) Toi, H.; Yamamoto, Y.; Sonoda, A.; Murahashi, S. *Tetrahedron* **1981**, *37*, 2261.

(20) Sun, Y.; Zhang, D.; Zhao, Z.; Zhai, Z.; Ma, Yuyuan.; Wang, Z.; Ma, Yiguan.; Li, D. *Shiyou Huagong* **1986**, *15*, 372.

(21) Chalk, A. J.; Wertheimer, V.; Magennis, S. A. *J. Mol. Catal.* **1983**, *19*, 189.

(22) Rennekamp, M. E.; Hoffman, M. K. *Org. Mass Spectrom.* **1975**, *10*, 1075.

(23) Badet, B.; Julia, M.; Mallet, J. M.; Schmitz, C. *Tetrahedron Lett.* **1983**, *24*, 4331.

(24) Shono, T.; Nishiguchi, I.; Ohmizu, H.; Itani, M. *J. Am. Chem. Soc.* **1978**, *100*, 545.