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Solvolysis of 1,1-Dimethyl-4-Alkenyl Chlorides: Evidence for π-Participation

Ivica Malnar,[†] Sandra Jurić,[†] Valerije Vrček,[†] Željka Gjuranović,[†] Zlatko Mihalić,[‡] and
Olga Kronja[*,†]

Faculty of Pharmacy and Biochemistry, Department of Chemistry, University of Zagreb,
A. Kovačića 1, P.O. Box 156, 10000 Zagreb, Croatia, and Faculty of Science, Department of Chemistry,
University of Zagreb, Strossmayerov trg 14, 10000 Zagreb, Croatia

kronja@rudjer.irb.hr

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Tertiary 1,1-dimethyl-4-alkenyl chloride (**1**) solvolyzes with significantly reduced secondary β-deuterium kinetic isotope effect (substrate with two trideuteromethyl groups) and has a lower entropy and enthalpy of activation than the referent saturated analogue **4** ($k_H/k_D = 1.30 \pm 0.03$ vs $k_H/k_D = 1.79 \pm 0.01$; $\Delta\Delta H^{\ddagger} = -9$ kJ mol^{-1}, $\Delta\Delta S^{\ddagger} = -36$ J mol^{-1} K^{-1}, in 80% v/v aqueous ethanol), indicating participation of the double bond in the rate-determining step. Transition structure **1-TS** computed at the MP2(fc)/6-31G(d) level of theory revealed that the reaction proceeds through a late transition state with considerably pronounced double bond participation and a substantially cleaved C−Cl bond. The doubly unsaturated compound **3** (1,1-dimethyl-4,8-alkadienyl chloride) solvolyzes with further reduction of the isotope effect, and a drastically lower entropy of activation ($k_H/k_D = 1.14 \pm 0.01$; $\Delta S^{\ddagger} = -152 \pm 12$ J mol^{-1} K^{-1}, in 80% v/v aqueous ethanol), suggesting that the solvolysis of **3** proceeds by way of extended π-participation, i.e., the assistance of both double bonds in the rate-determining step.

Introduction

A remote double bond which is appropriately placed toward the reaction center participates in solvolytic reactions.[1] The assistance can result in reduction of the secondary α- and β-deuterium kinetic isotope effects (KIEs),[2] in enhancement of the solvolytic reactivity,[3] in formation of cyclic products,[4] or in lowering the slope of the Hammett $\rho\sigma$ plot,[5] etc. There are many results published supporting allyl and homoallyl participation in solvolysis. Solvolysis of substrates with a double bond at C5 from the reaction center often proceed by way of anchimeric assistance, forming six-membered rings.[4,6] However, if the double bond is placed at C4 relative to the reaction center, in most of the cases no evidence of π-participation is reported, i.e., k_S is considered more favorable than the k_Δ process. For example, Bartlett demonstrated that in the acetolysis of 5-hexenyl *p*-nitrobenzoate, six-membered cyclic products were isolated and the reaction was enhanced in comparison with its saturated analogue, while in the same reaction with 4-pentenyl *p*-nitrobenzoate neither rate effect occurred, nor were cyclized products found.[4a] However, there are still a few ambiguous results in which π-participation cannot be excluded. Thus, Berson showed that in acetolysis of 7-norbornenyl brosylate the formation of the tricyclic products could be rationalized only if assistance of the double bond was taken into account.[7] Van Tamelen found 10% of the cyclopentane derivative when 2,3-epoxynorsqualene was subjected to acid-catalyzed reaction.[8] Even though the authors suggest that the process is very likely S_N1-like epoxy-ring opening, followed by interaction of the resulting carbocation with the neighboring π-electrons, a π-participation mechanism cannot be ruled out.

In our previous communication we showed that, surprisingly, the tertiary chloride **1** had considerably reduced secondary β-deuterium KIEs in solvolysis ($k_H/k_D = 1.30 \pm 0.03$, in 80% v/v aqueous ethanol, 80E; $k_H/k_D = 1.29 \pm 0.02$, in 97% wt/wt aqueous 2,2,2-trifluoroethanol, 97T) compared to its saturated analogue **4** ($k_H/k_D = 1.79 \pm 0.01$, 80E; $k_H/k_D = 1.81 \pm 0.01$, 97T), demonstrating

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[*] Tel: +385 1 4818 301. Fax: +385 1 4856 201.

[†] Faculty of Pharmacy and Biochemistry.

[‡] Faculty of Science.

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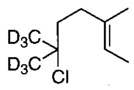
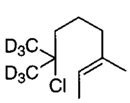

1-d_6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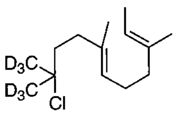
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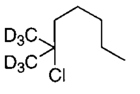
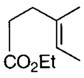

4-d_6

the assistance of the double bond in the rate-determining step.[9] Even more surprising was that the KIE observed for **1** was smaller than the secondary β-deuterium KIE obtained for chloride **2** ($k_H/k_D = 1.37 \pm 0.03$; 80E), in which the assistance of the double bond has been proven without ambiguity.[10] We proposed the result to be rationalized in terms of charge distribution in the reaction transition state. Thus, in the case of **1**, the transition state may be more akin to a tertiary cyclopentyl cation with relatively less charge at the C2, i.e., a "late" transition state.

To search for a possible participation of the double bond located at C4 from the reaction center, and for an extended π-participation with the doubly unsaturated substrate in which the first double bond is at C4 from the reaction center, we chose to examine the solvolytic behavior of protio and hexadeuterated chlorides **1** and **3**. Quantum chemical calculations at the MP2(fc)/6-31G(d) level of theory were also performed to gain an information about the transition states of the reactions investigated.

Results

Substrate Preparation. The protio and hexadeuterated isotopomers of chlorides **1**, **3**, and **4** were prepared by chlorination ($SOCl_2$) of the parent alcohols. The unsaturated parent alcohols of **1**, and **3**, and their hexadeuterated analogues were obtained by Grignard addition of CH_3I or CD_3I to esters **5**, and **6**, respectively.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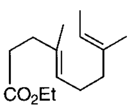
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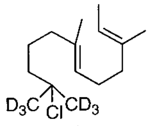
7-d_6

The *trans*-trisubstituted double bonds in both esters **5** and **6** were introduced according to the well-known Johnson procedure.[11] The saturated parent alcohol of **4** and its hexadeuterated analogue were prepared by addition of the Grignard reagent of 1-bromopentane to acetone and acetone-d_6, respectively. All synthetic procedures are presented in detail in the Experimental Section.

Kinetic Measurements. Chlorides **1**, **3**, and **4** and their hexadeuterated analogues **1**-d_6, **3**-d_6, and **4**-d_6 were subjected to solvolysis in 80% (v/v) aqueous ethanol (80E) and in 97% (w/w) aqueous 2,2,2-trifluoroethanol (97T). Solvolysis rates were followed by means of a pH-stat. The activation parameters were calculated from the rate constants determined at different temperatures. The rate constants and the activation parameters are presented in Table 1, while the secondary β-deuterium KIEs are given in Table 2.

Table 1. Solvolysis Rate Constants and Activation Parameters for 1,1-Dimethyl-1-alkyl and 1,1-Dimethyl-1-alk-4-enyl Chlorides

compd	solvent[a]	t, °C	k, 10^{-4} s^{-1}[b]	k_u/k_s[c]	$\Delta G^{\neq}$, kJ mol^{-1}[d]	$\Delta S^{\neq}$, J K^{-1} mol^{-1}[d]
4	80E	25	0.144[e]	-	91 ± 4[e]	-31 ± 13[e]
	97T	50	73.5 (6)	-	78 ± 4	-45 ± 12
		45	34.6 (6)			
		40	25.2 (2)			
		35	14.10 (5)			
		30	8.78 (4)			
		25	5.67 (7)			
1	80E	65	4.84 (2)	0.6[f]	82 ± 3	-67 ± 10
		60	3.70 (10)			
		55	2.015 (8)			
		50	1.334 (19)			
		45	0.835 (34)			
		40	0.454 (11)			
		25	0.0932			
	97T	55	40.7 (1)	0.5[f]	72 ± 7	-70 ± 21
		50	34.9 (7)			
		45	15.62 (3)			
		40	13.31 (7)			
		35	6.31 (2)			
		30	4.89 (9)			
		25	2.75			
3	80E	60	4.28 (4)	3.7[g]	53 ± 4	-152 ± 12
		50	2.13 (9)			
		40	1.190 (7)			
		25	0.399	-		
	97T	50	19.1 (3)		56 ± 1	-123 ± 1
		40	9.45 (7)			
		30	4.48 (8)			
		25	3.03			

[a] 80E is 80% (v/v) aqueous ethanol, and 97T is 97% (w/w) aqueous 2,2,2-trifluoroethanol. [b] The uncertainty of the last reported figure (standard error) is shown in parentheses. The rate constants without standard errors are extrapolated values. [c] Rate constant of unsaturated vs the corresponding saturated chloride at 25 °C. [d] Uncertainties are standard deviations. [e] From ref 17. [f] The rate of **4** is taken as k_s. [g] The rate of the corresponding saturated analogue ($k = 0.108 \times 10^{-4}$ s^{-1}, ref 17).

Table 2. Secondary β-Deuterium Kinetic Isotope Effects of Some 1,1-Dimethylalkyl and 1,1-Dimethylalkenyl Chlorides at 50 °C

substrate	solvent[a]	t, °C	k_H/k_D[b]
4[c]	80E	50	1.79 (1) 1.81 (1)
1	80E	50	1.30 (3)
	97T	30	1.29 (2)
2[d]	80E	50	1.37 (3)
3	80E	50	1.14 (1)
	97T	30	1.17 (2)
7[e]	80E	50	1.01 (4)

[a] 80E is 80% v/v aqueus ethanol; 97T is 97% w/w aqueous 2,2,2-trifluoroethanol. [b] The uncertainties of the last reported figure (standard deviation of the mean) are shown in parentheses. [c] Reference 9. [d] Reference 10. [e] Reference 18.

Computational Methods. Geometries were fully optimized and stationary points were characterized as minima (no imaginary frequencies) or as transition structures (one imaginary frequency) by calculation of the harmonic vibration frequencies. MP2(fc) calculations were carried out with the GAMESS program,[12] employing

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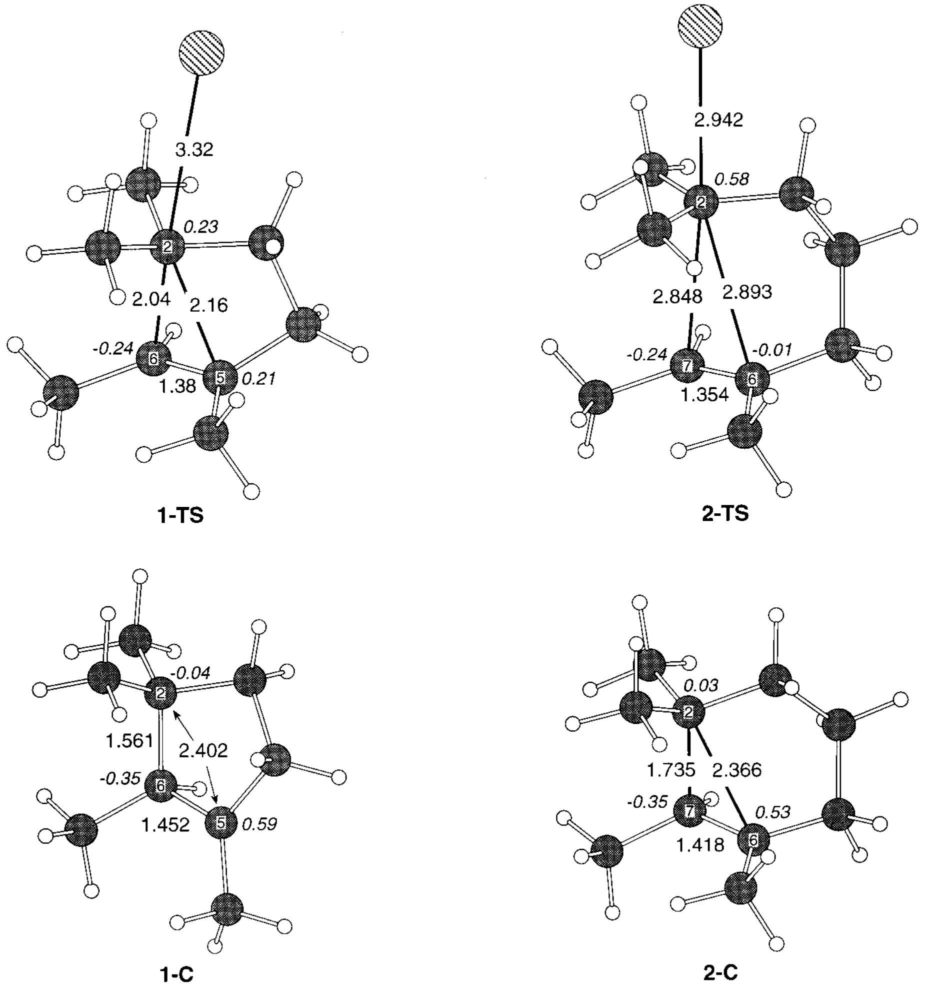

1-TS **2-TS**

1-C **2-C**

Figure 1. Optimized geometries at MP2(fc)/6-31G(d) of transition structures **1-TS** and **2-TS** and carbocation intermediates **1-C** and **2-C** with some important bond lengths and NBO charges (shown in italics).

6-31G(d) basis set.[13] IRC analysis confirmed that the transition structure located on the energy surface belongs to the chloride displacement reaction. Atomic charges were calculated at the MP2(fc)/6-31G(d) level of theory by a natural population analysis with the NBO program[14] built in Gaussian 94.[15]

The processes of formation of the carbocation intermediates from chlorides **1** and **2** were computed considering that the heterolytic cleavage of the C−Cl bond is accompanied by the backside interaction with the neighboring double bond. The energy minimum structures of chlorides **1** and **2** and the corresponding carbocations **1-C** and **2-C** were found as a stationary points. Also, the transition structures **1-TS** and **2-TS** were located on the energy surface. Optimization of **1-TS** was difficult because of the potential energy surface flatness in the vicinity of the transition structure. In both transition structures the imaginary frequency is associated with the dissociation of the C−Cl bond and simultaneous approach of the double bond. The transition structures **1-TS** and **2-TS** and the corresponding carbocation intermediates **1-C** and **2-C** are presented in Figure 1, accompanied with some important parameters (bond length and NBO charges).

To test the solvation effects on the computed structures, single-point self-consistent reaction field (SCRF) calculations with a polarized continuum model (PCM) were performed at the MP2/6-31G(d) level of theory.[16] A value of $\epsilon = 30$ was used as an input parameter for a solvent relative permittivity.

Product Analysis. The protio derivative of chloride **1** and the protio derivative of referent chloride **2** were subjected to ethanolysis in 80E in the presence of 2,4,6-collidine at 25 °C during about 10 halftimes of the reaction. According to GC analysis, the mixture of the products isolated consisted of three compounds. The mixture was separated by column chromatography and the products were characterized (Scheme 1). Ethanolysis of the chloride **1** yielded acyclic olefinic alcohol **8** (42%), and two acyclic unsaturated hydrocarbons **9** (39%) and

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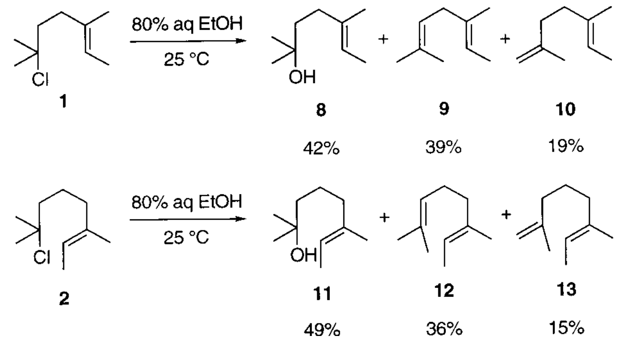
Scheme 1



10 (19%), while chloride **2** produced olefinic alcohol **11** (49%) and two acyclic olefinic products **12** (36%) and **13** (15%), respectively.

Discussion

It has been proven in numerous cases that only a large rate enhancement of the unsaturated compound in comparison with the saturated analogue ($k_U/k_S \gg 1$) can be taken as a valid proof of neighboring group participation.[10] Modest or even inverse rate effects can conceal some considerable assistance, and if this is a case, the participation or its lack must be proven by other methods. Solvolytic behavior of the tertiary chlorides **1** and **3** is such an example where the relative rates obtained are not decisive parameters (Table 1). Therefore, let us first establish the referent values of the parameters used here as reliable criteria in distinguishing the π-participation mechanism (k_Δ) (simple or extended) from the double bond unassisted process (k_S), the entropy ($\Delta S^\ddagger$) and the enthalpy of activation ($\Delta H^\ddagger$), and the secondary β-deuterium KIE. The later is the most reliable parameter.

Solvolysis of the saturated chloride **4**, as other numerous tertiary chlorides, proceeds by way of k_S process, in which nucleophilic solvation occur.[17] Thus, the corresponding activation parameters and the β-deuterium KIE (with **4**-d_6) represent the referent values for the mechanism unassisted by double bond(s) (Tables 1 and 2). These values can be used not only to compare the results obtained for chloride **1** but also for chloride **3**, since, regardless of the chain length, essentially the same values of activation parameters ($\Delta H^\ddagger \approx 90$ kJ mol^{-1}, $\Delta S^\ddagger \approx -30$ J K^{-1} mol^{-1}; 80E) and exactly the same values of secondary β-deuterium KIEs ($k_H/k_D \approx 1.8$; hexadeuterated at methyl groups adjacent to the reaction center) were obtained in solvolysis of numerous dimethylalkyl chlorides in which the alkyl group varied form ethyl to squalanyl.[10,18] This typical value of the β-deuterium KIE for the k_S process is due to the rate depression for the deuterated isotopomer caused by hyperconjugative electron release from the neighboring C−H(D) bond to the incipient empty p orbital in the transition state.

In a reaction in which the π-participation mechanism is operative, a lowering of $\Delta H^\ddagger$ occurs as a consequence of charge delocalization in the transition state. Delocalization inevitably involves bridging in the transition state, which causes a conversion of some internal rotations to more stiff vibrations. The outcome is the lower entropy relative to the ground state. Because of the charge delocalization, less hyperconjugative interaction between the p orbital of the reaction center and the β-CH(D) bonds of the methyl group occurs, resulting in a lower secondary β-deuterium KIE.

The activation parameters of the unsaturated tertiary chloride **2** are taken as the referent values for the simple π-participation mechanism.[10] The lower values for **2** compared with **4** ($\Delta\Delta H^\ddagger = -17$ kJ mol^{-1}; $\Delta\Delta S^\ddagger = -33$ J mol^{-1} K^{-1}; 80E)[19] are consistent with the mechanism involving a two π-electron assistance. Also, chloride **2** solvolyzes with a lower secondary β-deuterium KIE than the referent chloride **4** ($k_H/k_D = 1.37 \pm 0.03$ vs $k_H/k_D = 1.79 \pm 0.01$; 80E, Table 2) demonstrating that the partial positive charge located on the reaction center in the transition state is smaller.

Finally, the parameters of the doubly unsaturated tertiary chloride **7** are the referent values for the extended π-participation mechanism, in which more extensive charge delocalization (in comparison with **2**) results in further lowering of the enthalpy of activation ($\Delta H^\ddagger = 64 \pm 2$ kJ mol^{-1}) and the entropy of activation ($\Delta S^\ddagger = -118 \pm 6$ J mol^{-1}K^{-1}).[20] In addition, extended π-participation can cause larger volume contraction (-24.0 ± 0.5 cm^3 mol^{-1} for doubly unsaturated vs -13.3 ± 1.0 cm^3 mol^{-1} for the benzylic chloride with one double bond closely related to **7**).[11a] Nevertheless, the most significant result is the lack of secondary β-deuterium KIE in solvolysis of **7** ($k_H/k_D = 1.01 \pm 0.04$; 80E, Table 2), indicating that the hyperconjugative interaction is negligible, due to the extensive delocalization of the orbital vacancy from the reaction center.

Simple π-Participation. The activation parameters reported in Table 1 for ethanolysis of chloride show the same trend in comparison with the corresponding values for **4** as those for referent chloride **2**, demonstrating that the double bond has an important role in the rate-determining step in solvolysis. Chloride **1** solvolyzes with litlle more reduced β-deuterium KIE than the referent chloride **2** ($k_H/k_D = 1.30$ vs $k_H/k_D = 1.37$; 80E, Table 2). If that difference between the two effects is real, it could indicate more effective delocalization of the positive charge from the reaction center.

The computed transition state structures are in accord with the conclusion about an important role of the double bond in the rate-determining step. According to both transition state model **1-TS** and the referent model **2-TS**, the assistance of the double bond results in the formation of the three-centered bond in which a considerable weak and elongated C−Cl bonds exists. The principal difference between structures **1-TS** and the referent **2-TS** originates from the degree of the double bond assistance. In **1-TS** the interatomic distances C2−C5 and C2−C6 are shorter than distances C2−C6 snd C2−C7 in **2-TS**, while the C−Cl bond in **2-TS** is shorter than in **1-TS** (Figure 1). As was concluded on the basis of the β-deuterium KIE in a previous communication,[9] the computed structures clearly support that solvolysis of chloride **1** proceeds through a “later” transition state than the solvolysis of chloride **2**. According to NBO charges, in both transition

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structures **1-TS** and **2-TS**, a positive charge on the reaction center C2 is the largest.

In calculated carbocation intermediates **1-C** and **2-C** the positive charge is mainly transferred to the tertiary carbon atomcs C5 and C6, respectively (Figure 1). Similarly as in the transition structures, the C2−C5 and C2−C6 distances are shorter in **1-C** than the corresponding C2−C6 and C2−C7 distances in **2-C**. Nevertheless, because of the removal of the positive charge from the reaction center, cyclized product would be expected, which is not a case. Despite the theoretical findings, the lack of the cyclized products is not surprising. That discrepancy comes from the fact that the solvolyses were carried out in highly polar solvents (80E and 97T), while all reported calculations are for the isolated ion in the gas phase. The solvation effect on all species is not equally important. While the solvation of the starting chloride is not significant, the solvation of the positively charged intermediate is very pronounced. Consequently, the difference between the computed carbocation structure in the gas phase and under experimental conditions is the largest. The results obtained by theoretical calculation (SCRF=PCM model at the MP2/6-31G(d) level) clearly support the above assumption about the importance of the solvation effect in the transition state. In both cases solvation effects are negligible with chlorides **1** and **2** (ΔG_{solv} under 1 kcal/mol), while the transition states **1-TS** and **2-TS** are stabilized for 27 and 19 kcal/mol, respectively. Similar trends were recently obtained by Sorensen et al. in solvation simulation calculations for the camphenyl and other reference systems.[21] It is well-known that the ion pairs play an important role in such reactions, so the large fraction of elimination products might be rationalized if the basicity of the chloride ion is considered. The chloride can act as a base and eliminate the hydrogen in its vicinity, yielding the elimination instead of the cyclized products.

Extended π-Participation. The values of activation parameters and β-deuterium KIE of **3** show that its solvolytic behavior is different than that of **1** (and **2**), indicating a different reaction mechanism in the solvolysis of **3**. Let us examine how the results obtained would fit if it is presumed that both double bonds take part in the rate-determining step. Extended π-electron delocalization should cause further lowering of $\Delta H^{\ddagger}$, which is the case (Table 1). The presumed extended π-participation mechanism requires a certain conformation in the transition state, which demands a considerably high degree of order, and therefore a very negative $\Delta S^{\ddagger}$. Both values of $\Delta S^{\ddagger}$ obtained for **3** ($\Delta S^{\ddagger} = -152 \pm 12$ J mol^{-1} K^{-1}, 80E; $\Delta S^{\ddagger} = -123 \pm 1$ J mol^{-1} K^{-1}, 97T) and for **7** ($\Delta S^{\ddagger} = -118 \pm 6$ J mol^{-1} K^{-1}; 80E)[18] are dramatically reduced in comparison with the $\Delta S^{\ddagger}$ for the corresponding chlorides **1** and **2**, respectively. If the second double bond takes part in solvolysis of **3**, the largest contribution in decreasing the value of $\Delta S^{\ddagger}$ compared with **1** is caused by the loss of three internal rotations around the three single C−C bonds located between the two double bonds in the side chain of **3**. The extended π-participation mechanism fits excellently with the values of $\Delta S^{\ddagger}$, since it is known that the loss of one internal rotation in the transition state decreases $\Delta S^{\ddagger}$ by 15−20 J mol^{-1} K^{-1}.[1c,22]

The value of the most reliable parameter for **3**, the secondary β-deuterium KIE, is considerably smaller than that observed for the simple π-participation of **1** but is larger than the KIE obtained for the referent chloride **7**. Considering that the KIE is here interpreted as a measure of the charge on the reaction center in the transition state (methyl groups adjacent to the reaction center have free rotation), it can be concluded that the partial charge on the reaction center (C2) in **3-TS** is substantially lower than in **1-TS**, but it is also larger than the charge on the reaction center in the referent **7-TS**.

The results obtained in the solvolysis of **3** indicate that both double bonds take part in the rate-determining step in the solvolysis of **3**. However, the charge in **3-TS** is distributed differently than in **7-TS**, i.e., the carbon C2 is more positively charged than in the referent **7-TS**. Efficient charge delocalization could occur from the optimal preorganized structure, which cannot probably be achieved in **3-TS** because of the angle strain (between C1, C2, C3, and C4). Similar angle strain is negligible in **7-TS** in which the corresponding ring is five-membered. Therefore, in solvolysis of the model **7**, the participation of the second double bond is more important, the positive charge is more effectively delocalized, and **7** solvolyzes with a smaller β-deuterium KIE than **3**. The results obtained could also be interpreted in terms of “early” and “late” transition states. Unlike with the monounsaturated models, the “earlier” transition state exists in the case of **3** and the “later” in the case of **7**.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer using $CDCl_3$ as solvent, and IR spectra were recorded on neat compounds.

Esters **5** and **6** were prepared according to the procedures described by le Noble et al.,[11a] which include Johnson’s introduction of *trans*-trisubstituted double bond(s).[11b]

2,5-Dimethyl-5(*E*)-hepten-2-ol. The Grignard reagent, prepared from Mg (1.2 g, 50 mmol) and methyl iodide (7.1 g, 50 mmol) in THF (15 mL), was cooled to 0 °C, and the solution of ethyl 4-methyl-4(*E*)-hexenoate (**5**) (3.88 g, 25 mmol) in 20 mL of THF was added dropwise. The stirring was continued at room temperature for 1 h. The Grignard complex was hydrolyzed with saturated aqueous NH_4Cl. The water layer was washed with ether three times, and the combined ether layers were washed with brine and dried over Na_2SO_4. The crude product was distilled under reduced pressure yielding, 1.36 g (38%) of the pure product. IR 3370 cm^{-1} (b, O−H); ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 6H), 1.54−1.62 (m, 6H), 2.03−2.09 (m, 4H), 5.25−5.27 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.76, 15.57, 29.45, 34.3, 41.81, 70.93, 118.28, 135.94.

1,1,1-*d*$_3$-2,2,2-*d*$_3$-Methyl-5-methyl-5(*E*)-hepten-2-ol. The procedure is the same as described above. From Mg (0.17 g, 7 mmol), iodomethane-*d*$_3$ (1 g, 7 mmol), and ethyl 4-methyl-4(*E*)-hexenoate (ester **5**) (0.55 g, 3.5 mmol), 0.24 g (46%) of product was obtained. ^{1}H NMR ($CDCl_3$) δ 1.40−1.73 (m, 6H), 2.03−2.09 (m, 4H), 5.20−5.26 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.05, 15.42, 34.18, 34.43, 41.65, 70.54, 118.25, 136.04.

2,5,9-Trimethyl-5(*E*),9(*E*)-undecadien-2-ol. The Grignard reagent obtained from Mg (2.0 g, 82.3 mmol) and iodomethane (6.0 g, 42 mmol) in ether (15 mL) was cooled to 0 °C, and ethyl 4,8-dimethyl-4(*E*),8(*E*)-decadienoate (ester **6**) (2.4 g, 10.7 mmol) in ether (20 mL) was added dropwise. The reaction mixture was heated under reflux (1−2 h). The Grignard complex was hydrolyzed with saturated aqueous NH_4Cl, and the product was extracted with ether. The combined ether layers were dried over Na_2SO_4, the solvent was evaporated, and the crude product was purified by column chromatography on silica gel (petroleum ether/dichloromethane 3:1 followed by petroleum ether/dichloromethane 1:1). The

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[22] Page, M. I. *Chem. Soc. Rev.* **1973**, 295−323.

pure alcohol obtained (1.58 g, 79%) was in the form of a viscous oil. IR (neat) 3370 cm^{-1} (b, O−H); ^{1}H NMR (CDCl$_3$) δ 1.22 (s, 6H), 1.56−1.62 (m, 9H), 1.99−2.08 (m, 8H), 5.16−5.22 (m, 2H); ^{13}C NMR (CDCl$_3$) δ 13.07, 15.36, 15.76, 28.94, 26.32, 34.30, 39.39, 41.67, 70.99, 118.33, 124.39, 135.32, 135.58.

1,1,1-*d*$_3$-2,2,2-*d*$_3$-Methyl-5,9-dimethyl-5(*E*),9(*E*)-undecadien-2-ol. The procedure is the same as described for the protio analogue above. From Mg (2.0 g, 82.3 mmol), iodomethane-*d*$_3$ (6.0 g 41.4 mmol), and ethyl 4,8-dimethyl-4(*E*),8-(*E*)-decadienoate (2.4 g, 10.7 mmol), 1.57 g (68%) of pure alcohol was obtained. ^{1}H NMR (CDCl$_3$) δ 1.40−1.73 (m, 6H), 2.03−2.09 (m, 4H), 5.20−5.26 (m, 1H); ^{13}C NMR (CDCl$_3$) δ 13.05, 15.42, 34.18, 34.43, 41.65, 70.54, 118.25, 136.04.

1,1,1-*d*$_3$-2,2,2-*d*$_3$-Methyl-2-heptanol. The procedure is the same as described for the protio analogue above. From Mg (0.56 g, 23 mmol), 1-bromopentane (3.47 g, 23 mmol), and acetone-*d*$_6$ (1.47 g, 23 mmol), 2.43 g (78%) of pure alcohol was obtained: ^{1}H NMR (CDCl$_3$) δ 0.96 (t, 3H), 1.16−1.59 (m, 8H); ^{13}C NMR (CDCl$_3$) δ 22.35, 27.62, 27.71, 30.41, 34.67, 43.88, 63.06.

Chlorides 1, 3, and 4. 2-Chloro-2,5-dimethyl-5(*E*)-heptene (**1**), 2-chloro-1,1,1-*d*$_3$-2,2,2-*d*$_3$-methyl-5-methyl-5(*E*)-heptene (**1**-*d*$_6$), 2-chloro-2,5,9-trimethyl-5(*E*),9(*E*)-undecadiene (**3**), 2-chloro-1,1,1-*d*$_3$-2,2,2-*d*$_3$-methyl-5,9-dimethyl-5(*E*),9(*E*)-undecadiene (**3**-*d*$_6$), 2-chloro-2-methylheptane (**4**), and 2-chloro-1,1,1-*d*$_3$-2,2,2-*d*$_3$-methylheptane (**4**-*d*$_6$) were prepared from the corresponding alcohols and SOCl$_2$. Alcohol was dissolved in 10−15 mL of petroleum ether (bp 40−60 °C), and SOCl$_2$ was added dropwise at −15 °C. The reaction mixture was stirred for 2 h under reduced pressure (ca. 520−560 mmHg), to remove the liberated HCl and SO$_2$. The solvent was evaporated and crude chloride was used for kinetic measurements. Further purification proved to be unnecessary since the solvolysis rates were found to be independent of contamination.

Kinetic Measurements. Solvolysis rates were followed in 80% (v/v) aqueous ethanol (80E) and 97% wt/wt aqueous 2,2,2-trifluoroethanol (97T) titrimetrically by means of a pH-stat (end-point titration, pH = 6.85). Typically, 0.02 mmol of the chloride **1** was dissolved in 20 mL of the solvent at the required temperature thermostated ±0.05 °C, and the liberated HCl was continuously titrated by using a 0.008 M solution of NaOH in the same solvent mixture. Individual measurements could be described by the first-order low from 15% up to at least 80% completion. First-order rate constants were calculated from about 100 determinations by using a nonlinear least-squares program. Measurements were usually repeated 3−7 times. Activation parameters were calculated from rate constants at three different temperatures.

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Supporting Information Available: Coordinates for transition structures **1-TS** and **2-TS** and carbocations **1-C** and **2-C** optimized at the MP2(fc)/6-31G(d) level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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