mixture refluxed until complete solution of magnesium. A solution of 10.97 g (0.05 mol) of *p*-bromobenzoyl chloride in 10 mL of ether was then added and the reaction mixture refluxed for an additional 30 min. After the mixture was cooled and acidified with dilute sulfuric acid, the product was extracted several times with ether. The extract was dried with $CaSO_4$, the solvent evaporated, the residue dissolved in 100 mL of toluene, 0.43 g of *p*-toluenesulfonic acid added, and the mixture refluxed until the evolution of CO_2 ceased. The toluene solution was then washed with a 20% solution of potassium carbonate and several times with water and dried over $CaSO_4$, the solvent evaporated, and the residue distilled in vacuo. The product was recrystallized from methanol and redistilled at 1 mmHg. The yield was 48% (6.2 g) and ranged between 45–55% for the other title compounds. Melting points were as follows: *p*-Br, 54–56 °C; *p*-Cl, 49–51 °C; *p*-F, 26–28 °C; *p*-OCH_3, 42–44 °C. Boiling points were as follows: H, 140–145 °C (14 mmHg); *p*-CH_3, 116–118 °C (14 mmHg). All compounds gave satisfactory elemental C and H analyses and spectra (IR, NMR) consistent with their structures.

1-Aryl-*2,2-d*$_2$-4-methoxy-1-butanones. The title compounds were all prepared by the procedure described for the *p*-bromophenyl compound. 1-(*p*-Bromophenyl)-4-methoxy-1-pentanone (2 g, 7.8 mmol) was dissolved in 3.5 mL of dioxane containing 1 mL of D_2O and 0.05 mL of redistilled triethylamine and the mixture refluxed overnight. The solvent was then evaporated and the residue dissolved in the same amount of fresh solvent. After four exchanges, the product was distilled at 1 mmHg. The yield was 89% (1.8 g); mp 54–56 °C.

1-Aryl-4-methoxy-1-butanols. The title compounds were prepared by reduction of the corresponding ketones with either $LiAlH_4$ or $LiAlD_4$ in ether and conversion of the resulting carbinol into the chloride with thionyl chloride. Both reactions were carried out in the usual way. The products were distilled twice on a vacuum line and gave 96–99% of the theoretical amount of HCl upon solvolysis. The yields based on ketones were 78–85%. The spectra (IR, NMR) of the chlorides were consistent with their structures.

1-(*p*-Methoxyphenyl)-1-hexyl Chloride and Deuterated Analogues. Chlorides were prepared from carbinols with thionyl chloride in the usual way. Carbinols were prepared from the corresponding *p*-methoxybenzaldehyde and a Grignard reagent of *n*-hexyl bromide.[4] The preparation of deuterated reagents was completely analogous to that described in the synthesis of *trans*-1-chloro-5-methyl-1-aryl-5-heptenes.[17]

Acknowledgment. This work was supported by the Research Council of Croatia and Grant No. 02-011-1-(PL-480) administered by the National Institutes of Health.

Registry No. 3a ($R_1 = R_2 = H$), 71433-84-6; **3a**-*1-d* ($R_1 = D$; $R_2 = H$), 71433-85-7; **3a**-*2-d* ($R_1 = H$; $R_2 = D$), 71433-86-8; **3b** ($R_1 = R_2 = H$), 71433-87-9; **3b**-*1-d* ($R_1 = D$; $R_2 = H$), 71433-88-0; **3b**-*2-d* ($R_1 = H$, $R_2 = D$), 71433-89-1; **3c** ($R_1 = R_2 = H$), 71433-90-4; **3c**-*1-d* ($R_1 = D$; $R_2 = H$), 71433-91-5; **3d**-*2-d* ($R_1 = H$; $R_2 = D$), 71433-92-6; **3d** ($R_1 = R_2 = H$), 71433-93-7; **3d**-*1-d* ($R_1 = D$; $R_2 = H$), 71433-94-8; **3d**-*2-d* ($R_1 = H$; $R_2 = D$), 71433-95-9; **3e** ($R_1 = R_2 = H$), 71433-96-0; **3e**-*1-d* ($R_1 = D$; $R_2 = H$), 71433-97-1; **3e**-*2-d* ($R_1 = H$; $R_2 = D$), 71433-98-2; **3f** ($R_1 = R_2 = H$), 71433-99-3; **3f**-*1-d* ($R_1 = D$; $R_2 = H$), 71434-00-9; **3f**-*2-d* ($R_1 = H$; $R_2 = D$), 71434-01-0; **7**, 71434-02-1; **7**-*1-d*, 71434-03-2; **7**-*2-d*, 71434-04-3; di-*tert*-butyl (2-methoxyethyl)-malonate, 71434-05-4; diethyl (2-methoxyethyl)malonate, 6335-02-0; (2-methoxyethyl)malonic acid, 35841-35-1; isobutene, 115-11-7; *p*-methoxybenzoyl chloride, 100-07-2; *p*-methylbenzoyl chloride, 874-60-2; *p*-fluorobenzoyl chloride, 403-43-0; benzoyl chloride, 98-88-4; *p*-chlorobenzoyl chloride, 122-01-0; *p*-bromobenzoyl chloride, 586-75-4; 1-*p*-anisyl-4-methoxy-1-butanone, 71434-06-5; 1-*p*-tolyl-4-methoxy-1-butanone, 71434-07-6; 1-(*p*-fluorophenyl)-4-methoxy-1-butanone, 71434-08-7; 1-phenyl-4-methoxy-1-butanone, 34904-87-5; 1-(*p*-chlorophenyl)-4-methoxy-1-butanone, 64413-31-6; 1-(*p*-bromophenyl)-4-methoxy-1-butanone, 71434-09-8; 1-*p*-anisyl-*2,2-d*$_2$-4-methoxy-1-butanone, 71434-10-1; 1-*p*-tolyl-*2,2-d*$_2$-4-methoxy-1-butanone, 71434-11-2; 1-(*p*-fluorophenyl-*2,2-d*$_2$)-4-methoxy-1-butanone, 71434-12-3; 1-phenyl-*2,2-d*$_2$-4-methoxy-1-butanone, 71434-13-4; 1-(*p*-chlorophenyl-*2,2-d*$_2$)-4-methoxy-1-butanone, 71434-14-5; 1-(*p*-bromophenyl-*2,2-d*$_2$)-4-methoxy-1-butanone, 71434-15-6; *p*-methoxybenzaldehyde, 123-11-5; *n*-hexyl bromide, 111-25-1.

Secondary Deuterium Isotope Effects in Solvolysis of 1-Aryl-5-methyl-5-hepten-1-yl Chlorides. Comparison of π and n Participation Mechanisms

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Three series of deuterated compounds related to **1** were prepared and their solvolysis rates measured. Since the relative contribution of k_c and k_Δ to the observed solvolysis rates of **1** are known and since the isotope effects on the k_c route can be estimated, it is possible to extract from the data secondary deuterium isotope effects associated with the k_Δ process. In all cases, the α-deuterium isotope effects on k_Δ are reduced in magnitude as compared to those in the k_c process, which is consistent with bridging. β-Deuterium isotope effects on k_Δ are essentially nil which can be explained as being due to both conformational restrictions to hyperconjugative electron release from the C–D bonding orbitals caused by bridging and to charge delocalization away from the reaction center. Deuteration of the aliphatic double bond produces inverse isotope effects in all cases where anchimeric assistance is operative. The latter observation clearly demonstrates the direct involvement of the aliphatic double bond in the rate-determining step of the k_Δ process. A direct comparison of rates show that 1-aryl-4-methoxy-1-butyl chlorides **3** solvolyze slightly faster than the corresponding chlorides of the series **1**. The rate factors are, however, too small to confirm the possibility that n and π participations proceed by different mechanisms. If the aliphatic methoxyl group is directly involved in the rate-determining step of the k_Δ process throughout the series **3**, then measured isotope effects reflect transition-state structures with a variable amount of bridging, depending upon the solvent and/or the nature of the aromatic substituent.

It has been shown[2] that **1** solvolyzes, depending upon the nature of the substituent Y, from 0 to 98% by way of k_Δ. The anchimerically assisted route seems to proceed via charge-delocalized carbonium ions **2** rather than car-

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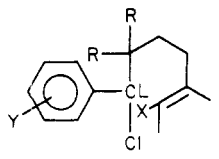
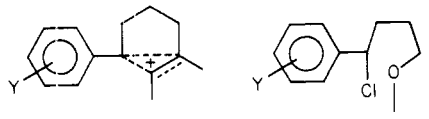


1, L = R = X = H
1-*1-d*, L = D; R = X = H
1-*2,2-d*$_2$, R = D; L = X = H
1-*6-d*, X = D; L = R = H

benium ions **5** with a fully formed new C_1–C_6 bond.[2b] The solvolysis of **3** has also been investigated,[3] and it was shown that it proceeds predominantly by way of methoxyl participation. Secondary deuterium isotope effects observed



2 3

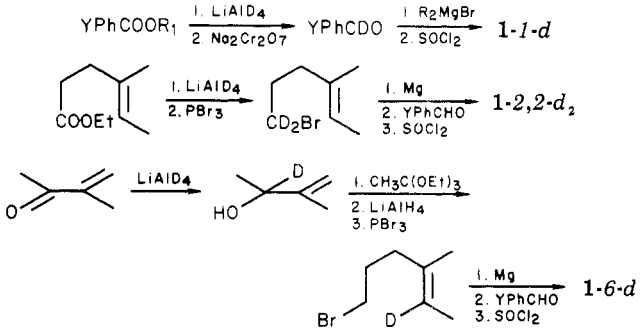
in reactions of **3** are best accommodated by assuming two distinct k_Δ pathways: an internal direct-displacement reaction of the chloride by the methoxyl or, alternatively, a rate-determining formation of an intimate ion pair followed by a fast formation of the bond between the methoxyl oxygen and the carbenium ion center.[4]

It seemed, therefore, of interest to obtain secondary deuterium isotope effects in the solvolysis of **1** and to compare them with those measured in the reactions of **3**. The results of this work are here reported.

Results

Three series of deuterated compounds 1-*1-d*, 1-*2,2-d*$_2$, and 1-*6-d* were prepared as shown in Scheme I and are described in the Experimental Section. Solvolysis rates were followed by continuous titration of the liberated acid by means of a pH stat, alternating deuterated and undeuterated substrates. Each individual measurement was repeated four to six times. Typically, 0.04 mmol of the chloride was dissolved in 20 mL of the solvent thermostated at ±0.05 °C and the liberated acid titrated with a 0.02 N solution of sodium alkoxide conjugate to the solvent. In all cases the first-order rate law was obeyed up to at least 80% reaction completion. First-order rate constants were calculated from points between 15–80% reaction by using a nonlinear least-squares program. The results are shown in Table I. The contributions of k_Δ to the total rate were known from previous work[2] and are shown in the last column of Table I as "percent" participation. The isotope effects obtained are shown in Table II. Isotope effects on the k_c process were estimated by using the measured values in solvolysis of 1-(*p*-methoxyphenyl)-1-hexyl chloride[3] and those in reactions of 1-arylethyl chlorides.[4] Since the relative contributions of k_Δ and k_c are known, it is possible to extract from the data the isotope effects on the pure k_Δ process. All relevant numbers are shown in Table II, except the α-deuterium isotope effects on k_c which should be k_H/k_D = 1.15 in all cases.[3,4]

Scheme I



R_1 = Et, Y = *p*-OCH_3 or *p*-CH_3, R_2 = 4-methyl-4-hexenyl residue; R_1 = H, Y = *p*-Br or *m*-Br; R_1 = Me, Y = H

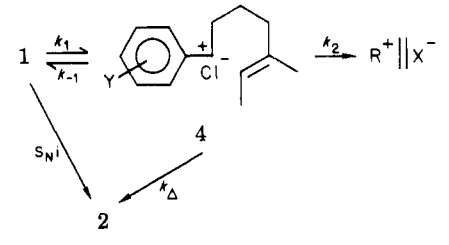
Discussion

The k_Δ process in solvolysis of **1** proceeds with involvement of the aliphatic double bond in the rate-determining step. This is clearly demonstrated by the following facts.

(1) Solvolysis rate enhancements relative to the chloride with a saturated aliphatic chain depend upon the degree of substitution at the double bond carbons. With no methyl groups at either C_5 or C_6, the solvolysis rates are practically not enhanced. One methyl at either C_5 or C_6 produces similar rate enhancements, and their product is equal to the rate accelerations observed with **1**.[2b]

(2) In all cases where rate enhancements are observed with **1**, deuteration of the double bond as in 1-*6-d* gives rise to inverse isotope effects.

By analogy to 1-arylethyl chlorides,[4] the k_c process, which competes with k_Δ in solvolysis of **1**, can be assumed to proceed by way of an intimate ion pair **4**, with the conversion of **4** into a solvent-separated ion pair representing the rate-determining step. A possible way for the



aliphatic double bond to accelerate the reaction rate would be by allowing a fast conversion of **4** into the carbonium ion **2** and making k_1 rate determining.

An analogous mechanism has been proposed for solvolysis of 3,3-dimethyl-2-butyl (pinacolyl) brosylate[5] and was also considered as a possible explanation for the observed isotope effects in solvolysis of **3**.[3] Such a mechanism, however, is clearly *not* operative with **1** since the double bond is not involved in k_1. The rate-determining step in the anchimerically assisted solvolysis of **1** must be either an internal direct displacement (S_Ni) leading directly from **1** to **2** or the conversion of the intimate ion pair **4** into the carbonium ion **2** (k_Δ).

α-Deuterium Isotope Effects. The isotope effects obtained for the k_Δ process in solvolysis of 1-*1-d* are all reduced in magnitude relative to the limiting maximum of k_H/k_D = 1.15 assumed for the k_c process.[4]

The α-deuterium isotope effect for a complete conversion of a C–Cl bond to a C–C bond can be obtained from H–D fractionation factors calculated by Shiner.[6] The

(1) (a) "Pliva" Pharmaceutical and Chemical Works. Taken in part from the Ph.D. Thesis of E.P., University of Zagreb, 1976. (b) Faculty of Pharmacy and Biochemistry.
(2) (a) E. Polla, S. Borčić, and D. E. Sunko, *Tetrahedron Lett.*, 799 (1975); (b) I. Mihel, M. Orlović, E. Polla, and S. Borčić, *J. Org. Chem.*, previous paper in this issue.
(3) I. Mihel, J. Šistek, K. Humski, S. Borčić, and D. E. Sunko, *J. Org. Chem.*, previous paper in this issue.
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(6) S. R. Hartshorn and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **94**, 9002 (1972).

Table I. Solvolysis Rates of 1-Aryl-5-methyl-5-heptenyl Chlorides and Deuterated Analogues

Y[a]	solvent[b]	T,[c] °C	10^5k_H,[d] s^{-1} (for 1)	10^5k_D,[d] s^{-1} 1-*1*-*d*	1-*2*,*2*-d_2	1-*6*-*d*	% particip[e]
p-OCH_3	95E	5.2	266 (2)	236 (4)	233 (1)	263 (1)	0
p-CH_3	95E	50.1	43.1 (1)	38.3 (5)	40.8 (6)	44.9 (9)	50
p-CH_3	80E	25	35.4 (3)	31.9 (4)	33.2 (1)	36.7 (5)	55
H	80E	50.2	23.1 (5)	21.4 (2)	22.2 (2)	25.4 (3)	82
p-Br	97T	25	157 (1)	144 (1)	158 (1)	169 (1)	95
m-Br	97T	25	23.6 (2)	21.4 (2)	22.9 (5)	25.5 (2)	98

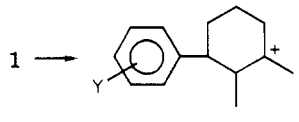
[a] Substituent on the phenyl ring. [b] 95E and 80E are 95 and 80 vol % aqueous ethanol, respectively, and 97T is 97 wt % 2,2,2-trifluoroethanol. [c] Temperatures are uncorrected, resulting in rate constants slightly different from those published in ref 2. [d] Numbers in parentheses are uncertainties of the last reported figure, i.e., 43.1 (1) = 43.1 ± 0.1. Uncertainties are standard deviations of the mean. [e] Calculated from rates reported in ref 2.

Table II. Solvolysis of 1-Aryl-5-methyl-5-heptenyl Chlorides. Isotope Effects[a]

Y[b]	solvent[c]	k_H/k_D[d] 1-*1*-*d*	1-*1*-*d*, k_Δ[e]	1-*2*,*2*-d_2	1-*2*,*2*-d_2, k_c[f]	1-*2*,*2*-d_2, k_Δ[e]	1-*6*-*d*	1-*6*-*d*, k_Δ[e]
p-OCH_3	95E	1.12 (2)		1.13 (1)	1.09		1.01 (1)	
p-CH_3	95E	1.14 (2)	1.12	1.06 (2)	1.15	0.97	0.96 (2)	0.91
	80E	1.11 (2)	1.08	1.07 (1)	1.15	0.99	0.97 (2)	0.93
H	80E	1.09 (3)	1.07	1.04 (2)	1.17	1.02	0.90 (2)	0.88
p-Br	97T	1.09 (1)	1.09	0.99 (1)	1.17	0.98	0.93 (1)	0.93
m-Br	97T	1.10 (1)	1.10	1.03 (2)	1.17	1.03	0.93 (1)	0.92

[a] All isotope effects are for 25 °C. When necessary, extrapolations from other temperatures were made by assuming normal temperatures dependence. In no case was the correction more than ±0.01. [b] Substituent on the phenyl ring. [c] 95E and 80E are 95 and 80 vol of ethanol, respectively, and 97T is 97 wt % of 2,2,2-trifluoroethanol. [d] Numbers in parentheses are uncertainties of the last reported figure, i.e., 1.12 (2) = 1.12 ± 0.02. Uncertainties are standard deviation of the mean. [e] Isotope effects on the pure k_Δ process. [f] Isotope effects on the pure k_c process.

α-deuterium isotope effect for breaking (making) a C–Cl bond should just be about equal to that associated with breaking (making) a C–C bond.[6] On these grounds, if 1 were directly transformed into 5 and if the transition state



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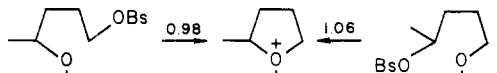
were adequately described by 5, an α-deuterium effect of unity should be expected. This is, however, an unrealistic estimate due to the following facts. Both **6P** and **6S** solvolyze through transition states closely resembling the common intermediate **7**.[7] The associated α-deuterium



6P **7** **6S**

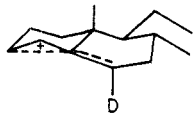
effects[8] (k_H/k_D per D atom at 25 °C) are shown above the arrows. The larger isotope effect associated with **6S**, a secondary substrate, is thought to be due to a slight vertical displacement of the transition state on a More-O'Ferrall–Jencks diagram relative to that for **6P**.[8] Since 1 is also a secondary substrate, the α-deuterium effect for a rate-determining conversion to 5 should be analogous to that observed with **6S** and not with **6P**. The limiting maximum effect for a sulfonate ester leaving group is 1.22,[9] so that **6S** reacts with an α-deuterium effect which is 33% larger than the minimum value observed with **6P**. The minimum α-deuterium effect for completely breaking a carbon–chlorine bond and completely making a carbon–carbon bond was calculated to be 1.00, while the limiting maximum effect for a chloride leaving group is 1.15.[4] Hence, by analogy to **6S**, a direct internal-displacement reaction leading from 1 to 5 should be associated with an α-deuterium effect of k_H/k_D = 1.05. The average of the observed values on the anchimerically assisted route is 1.09. Since 1 apparently does not solvolyze by way of the carbenium ion 5 but by way of carbonium ion **2**[2b] in which the bonding to the neighboring group is less than complete, the measured α-deuterium effects seem to be in accord with a mechanism involving a rate-determining direct conversion of 1 to 2. In solvolysis of 3 a consistent change in the magnitude of the α-deuterium effect with changing of the σ^+ value of the substituent Y and/or the ionizing power of the solvent was observed.[3] Such is not the case with 1-*1*-*d*, and the foregoing calculation might provide a rationale (besides the obvious one that the effects measured with 1-*1*-*d* are less accurate): the expected range of possible isotope effects with 3 might be much larger (0.99–1.15) than that in the case of 1 (1.09–1.15). Finally, it should be mentioned that the effects measured with 1-*1*-*d* could also be rationalized by the alternative mechanism involving the formation of the intimate ion pair 4 followed by a rate-determining conversion of 4 into 2.

β-Deuterium Isotope Effects. The isotope effects for the anchimerically assisted solvolysis of 1-*2*,*2*-d_2 are essentially nil throughout the series. If the reaction transition state resembles 2, this observation can be well understood[3,10] and can be explained as being due to the combined operation of two factors: (a) bridging to C_5 and C_6 forces the β-CD bonding orbitals into a position unfavorable for a hyperconjugative electron release to the reaction center,[11] and (b) the hyperconjugative electron demand of

(7) E. L. Allred and S. Winstein, *J. Am. Chem. Soc.*, **89**, 3991, 3998 (1967).
(8) R. Eliason, S. Borčić, and D. E. Sunko, *Croat. Chem. Acta*, **51**, 203 (1978).
(9) A. Streitwieser, Jr., and A. Dafforn, *Tetrahedron Lett.*, 1263 (1969).
(10) D. E. Sunko and S. Borčić, ref 5b, Chapter 3.
(11) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **83**, 240 (1961); p 147 of ref 5b.

the reaction center is drastically reduced due to charge delocalization to both the aryl ring[4] and aliphatic double bond.[10] The difference in the β effects observed on the k_c route between **1a** (1.13) and 1-(*p*-anisyl)-1-hexyl chloride (1.09) is probably real and might reflect a change in the conformation of the side chain in the transition state owing to different solvation requirements.

Remote Isotope Effects. Deuteration at the neighboring group as in 1-*6-d* is associated with inverse isotope effects in all cases where k_Δ is competitive with k_c and is nil if k_c is the only pathway of the solvolysis reaction. Similar remote isotope effects have been observed earlier in π-assisted solvolyses.[12,13] An inverse isotope effect could indicate an sp^2 to sp^3 rehybridization of the C–H(D) bonding orbitals at the deuterated site and is thus consistent with bridging. It should be pointed out, however, that the magnitude of that effect might not be a good measure for the strength of bonding between C_1 and C_6 at the reaction transition state. Thus, in solvolysis of deuterated 3-cholesteryl tosylate which proceeds by way of carbonium ion 8 an inverse isotope effect of 0.94 was



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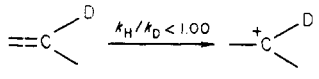
observed[13] although the reaction transition state cannot involve any bridging to the deuterated carbon.

It would seem that the transformation of an ethylenic carbon to a carbenium ion center is associated with an inverse isotope effect.



In any case, the observation of remote isotope effects clearly demonstrates that the aliphatic double bond is directly involved in the rate-determining step of the k_Δ process in solvolysis of 1.

Comparison of n and π Participation Mechanisms. It has been shown[3] that the isotope effects observed in solvolyses of 3, which proceed by way of n participation, can best be accommodated by assuming a dichotomy in the k_Δ route, as mentioned earlier in this discussion. On the other hand, the results of the present work clearly indicate that the rate enhancements observed in π participation with 1 cannot be due to a rate-determining formation of the intimate ion pair 4 (k_1) which would eliminate internal return (k_{-1}) associated with the k_c process (k_2 being rate determining). However, the results obtained with 3 are best explained if it is assumed that some of these chlorides react by just such a pathway.[3] Is it possible that π participation proceeds by a different mechanism than n participation? It should be possible to answer this question by comparing the reaction rates of 1 and 3. If with 1 the conversion of the intimate ion pair 4 into the carbonium ion 2 is rate determining, while with 3 the formation of the intimate ion is the slow step, 3 would be expected to react significantly faster than 1. Such a conclusion is reached on the reasonable assumption that k_1 cannot be much faster with 1 than with 3. The rate retardation on the ionization process due to the inductive effect of the methoxyl in 3 has been estimated[3] to amount to about a factor of 0.4. This conclusion is not modified by the inclusion of a possible displacement route leading directly from 1 and/or 3 to the cationic intermediate. In Table III, solvolysis rate constants for 1 and 3 are summarized for all cases in which the available data[2] allow a direct comparison. It can be seen that 3 reacts on the average only about twice as fast as 1. This rate factor is too small to serve as a distinguishing feature between n and π participation mechanisms. Moreover, in view of uncertainties encountered in the interpretation of experimental data obtained with 3 as discussed in the preceding paper, an alternative mechanism for n participation remains, therefore, a distinct possibility: the solvolysis of 3 could proceed by way of a direct involvement of the aliphatic methoxyl in the rate-determining step throughout the series. Observed isotope effects then indicate variable amounts of bridging in the transition states and possibly also in the cationic intermediates,[14] depending upon the solvent and the aryl substituent. It is also necessary to assume a nonlinear relation between the magnitude of the α-deuterium effect and the sum of the reacting bonds orders.[3,12]

Table III. Solvolysis Rate Constants of 1-Aryl-4-methoxy-1-butyl Chlorides (3) and of 1-Aryl-5-methyl-5-hepten-1-yl Chlorides (1)

Y[a]	solvent	T, °C	10^5k, s^{-1} 3[b]	10^5k, s^{-1} 1[c]	ratio of n/π
p-CH_3	95E	50	111	34.9	3.2
		40	40	14.6	2.7
	80E	25	67.7	28.1	2.4
H	80E	50	63.9	22.6	2.8
		25	4.43	2.34	1.9
p-Br	80E	50	16.7	6.38	2.6
	97T	25	67.5	193	0.35

[a] Substituent on the phenyl ring. [b] Data from ref 3. [c] Data from ref 2.

It is noteworthy that β-deuterium effects seem to be on the average about 3% lower for π participation with 1 than those for n participation with 3. This trend can be easily understood if k_Δ is assumed to be the slow step in the former and k_1 in the latter. A transition state resembling 2 requires severe conformational restrictions to hyperconjugative electron release from β-CD bonding orbitals, resulting in lower isotope effects than in a rate-determining ionization without significant bridging.

Experimental Section

Deuterium content in deuterated compounds was determined by mass spectrometry and was found to be >97% in all cases. All compounds gave spectra (IR, NMR) consistent with their structure.

1-Aryl-*1-d*-methanals. Deuterated substituted benzaldehydes were prepared from the corresponding α-deuterated benzyl alcohols by dichromate–sulfuric acid oxidation in Me_2SO described by Rao and Filler[15] in 55–80% yields.

***trans*-1-Bromo-4-methyl-4-hexene-*1,1-d*$_2$.** Ethyl *trans*-4-methyl-4-hexenoate[16] was reduced to the corresponding carbinol with lithium aluminum deuteride in ether. The primary alcohol was converted to the title compound with phosphorus tribromide in pyridine at low temperature[17] in 55% yield.

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3-Methyl-3-buten-2-*d*-2-ol. 3-Methyl-3-buten-2-one was reduced with lithium aluminum deuteride in ether to the carbinol in 35% yield.

***trans*-1-Bromo-4-methyl-4-hexene-5-*d*.** Ethyl *trans*-4-methyl-4-hexen-5-*d*-oate was prepared from 3-methyl-3-buten-2-*d*-2-ol and ethyl orthoacetate in 72% yield by the method of Johnson et al.[16] Reduction of the ester with lithium aluminum hydride followed by the reaction of the carbinol with phosphorus tribromide in pyridine at low temperature[17] gave the title compound.

***trans*-1-Aryl-5-methyl-5-hepten-1-ols.** The title compounds were prepared from the Grignard reagent of the corresponding *trans*-4-methyl-4-hexen-1-yl bromide and arylmethanals in 11–55% yields. A typical preparation is described.

To 480 mg (0.02 g-atom) of magnesium shavings covered with anhydrous ether was added a crystal of iodine followed by 3.54 g (0.02 mol) of *trans*-1-bromo-4-methyl-4-hexene in 20 mL of anhydrous ether. The addition was carried out with stirring and at room temperature. Stirring was continued until complete disappearance of magnesium (about 90 min). Benzaldehyde (2.12 g, 0.02 mol) in 15 mL of anhydrous ether was then added dropwise to the reaction mixture under stirring and cooling with ice and water. The stirring was continued for 2 h followed by addition of an ice-cold saturated aqueous solution of ammonium chloride. The product was then extracted from the reaction mixture several times with ether, the combined extracts were washed with water and dried over magnesium sulfate, the ether was evaporated, and the residue was distilled under reduced pressure. It was necessary to purify the product by high-pressure LC using a Porasil column and chloroform as the mobile phase. The yield was 1.81 g (44.3%).

***trans*-1-Chloro-1-aryl-5-methyl-5-heptenes.** A typical preparation is described. To a mixture of *trans*-1-phenyl-5-methyl-5-hepten-1-ol (408 mg, 2 mmol), anhydrous pyridine (0.194 mL), and anhydrous ether (5 mL) at −20 °C was added 0.176 mL (2.4 mmol) of freshly distilled thionyl chloride dropwise and with stirring. Stirring was continued at −15 to −20 °C for 45 min and the reaction mixture brought to room temperature. Pyridinium hydrochloride was then filtered off and the solvent and unreacted reagents removed in vacuo. Despite these precautions, the chlorides contained 10–30% of the elimination product. Further purification proved to be unnecessary since the solvolysis rates were found to be independent of the contamination.

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Registry No. 1-*1-d* (Y = *p*-OCH_3), 71434-98-5; 1-*1-d* (Y = *p*-CH_3), 71434-99-6; 1-*1-d* (Y = H), 71435-00-2; 1-*1-d* (Y = *p*-Br), 71435-01-3; 1-*1-d* (Y = *m*-Br), 71435-02-4; 1-*2,2-d_2* (Y = *p*-OCH_3), 71435-03-5; 1-*2,2-d_2* (Y = *p*-CH_3), 71435-04-6; 1-*2,2-d_2* (Y = H), 71435-05-7; 1-*2,2-d_2* (Y = *p*-Br), 71435-06-8; 1-*2,2-d_2* (Y = *m*-Br), 71435-07-9; 1-*6-d* (Y = *p*-OCH_3), 71435-08-0; 1-*6-d* (Y = *p*-CH_3), 71435-09-1; 1-*6-d* (Y = H), 71435-10-4; 1-*6-d* (Y = *p*-Br), 71435-11-5; 1-*6-d* (Y = *m*-Br), 71435-12-6; 1-(*p*-methoxyphenyl)-1-*d*-methanal, 19486-71-6; 1-(*p*-methylphenyl)-1-*d*-methanal, 13277-99-1; 1-phenyl-1-*d*-methanal, 3592-47-0; 1-(*p*-bromophenyl)-1-*d*-methanal, 42007-03-4; phenyl)-1-*d*-methanal, 71435-13-7; (*trans*)-1-bromo-4-methyl-4-hexene-*1,1-d_2*, 71435-14-8; ethyl (*trans*)-4-methyl-4-hexenoate, 58203-62-6; 3-methyl-3-buten-2-ol-2-*d*, 71435-15-9; 3-methyl-3-buten-2-one, 814-78-8; (*trans*)-1-bromo-4-methyl-4-hexene-*5-d*, 71435-16-0; ethyl *trans*-4-methyl-4-hexenoate-5-*d*, 71435-17-1; ethyl orthoacetate, 78-39-7; (*trans*)-1-(*p*-methoxyphenyl)-5-methyl-5-hepten-1-ol, 71435-18-2; (*trans*)-1-(*p*-methylphenyl)-5-methyl-5-hepten-1-ol, 71435-19-3; (*trans*)-1-phenyl-5-methyl-5-hepten-1-ol, 71435-20-6; (*trans*)-1-(*p*-bromophenyl)-5-methyl-5-hepten-1-ol, 71435-21-7; (*trans*)-1-(*m*-bromophenyl)-5-methyl-5-hepten-1-ol, 71435-22-8; (*trans*)-4-methyl-4-hexen-1-yl bromide, 71435-23-9; (*trans*)-1-chloro-1-(*p*-methoxyphenyl)-5-methyl-5-heptene, 56040-03-0; (*trans*)-1-chloro-1-(*p*-methylphenyl)-5-methyl-5-heptene, 56040-04-1; (*trans*)-1-chloro-1-phenyl-5-methyl-5-heptene, 56040-05-2; (*trans*)-1-chloro-1-(*p*-bromophenyl)-5-methyl-5-heptene, 56040-06-3; (*trans*)-1-chloro-1-(*m*-bromophenyl)-5-methyl-5-heptene, 56112-25-5.

Buffer Catalysis in the Hydrolysis of Picryl Chloride[1]

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The kinetics of the hydrolysis of picryl chloride were studied between pH 7.06 and 11.60 with different buffers at various concentrations. The reaction is strongly catalyzed by tertiary amines (*N*-ethylmorpholine, 2,4,6-trimethylpyridine, and Dabco) and also by carbonate and bicarbonate. A small increase in rate is also observed with phosphate trianion and borate. The catalysis seems to be of the nucleophilic type for *N*-ethylmorpholine, 2,4,6-trimethylpyridine, carbonate, and bicarbonate, but a mechanism involving general base-catalyzed addition of water is suggested for the other bases.

The mechanism of aromatic nucleophilic substitution of activated substrates has been extensively studied during the last 10 years.[2] Amines are probably the most studied nucleophiles and kinetic studies of their intra- or intermolecular reactions greatly contributed in firmly establishing the multistep nature of the mechanism.[3] In general terms, it can be described by Scheme I, where NuH represents any neutral nucleophile. In this scheme all the reaction paths identified at present are shown, but not all of them take place simultaneously. With many amines as nucleophiles the product-forming steps are rate determining, and general base catalysis through the I → II → IV → V pathway is observed. Specific base catalysis attributed to the pathway I → III → IV → V was reported in the reaction of imidazole with 2,4-dinitrofluorobenzene.[4] General base catalyzed addition of water to 4,6-dinitrobenzofuroxan,[5] which corresponds to the diagonal pathway I → IV in Scheme I, is the only known example where the formation of a Meisenheimer complex is general base catalyzed.

One reason why base catalysis of the addition step is not usually found could be that, under the conditions of the

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