Solvolysis Rates of Substituted 1-Phenyl-5-hexenyl Chlorides. Evidence for π Participation and Carbonium Ion Intermediates

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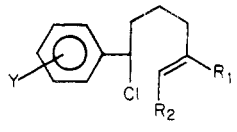
Received May 22, 1978

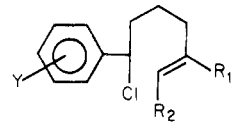
1-Aryl-5-alkenyl chlorides **1U**, **2U**, and **3U** and their analogues with a saturated aliphatic chain **1S**, **2S**, and **3S** were prepared and their solvolysis rates measured. The results are compared with those reported earlier for **4U** and **4S**. None of the *p*-anisyl-5-alkenyl chlorides nor any of the chlorides **1U** show appreciable rate enhancements relative to their analogues of the S series. Solvolysis rates of all other chlorides of the U series are accelerated. Rate enhancements are due to a negative $\Delta\Delta H^{\ddagger}$ overcompensating for a positive $\Delta\Delta S^{\ddagger}$, which is consistent with neighboring-group participation of the aliphatic double bond. From the data in the literature and the observed rate enhancements, the driving force for 5,6 π participation is calculated to amount to ca. 14 kcal/mol. Methyl substitution at C_6 (**3U**) is somewhat more effective in accelerating the reaction rate than that at C_5 (**2U**). Such behavior is consistent with the formation of charge-delocalized carbonium ions in the rate-determining step. $\rho^+\sigma^+$ correlation with **4U** suggests a change in mechanism from unassisted solvolysis (k_c) for the *p*-anisyl derivative to predominantly neighboring group assisted solvolysis (k_Δ) for all other substrates of the series. The large negative value of $\rho_\Delta{}^+$ (−3.94) indicates considerable benzylic resonance stabilization of the transition state in the k_Δ process. It is pointed out that the detection of a possible extended π participation in biomimetic olefinic polycyclizations requires closely matched saturated structures for comparison.

We have previously reported[2] that the solvolysis of the series of chlorides **4U** is enhanced relative to the corresponding chlorides **4S** with the saturated aliphatic chain. This case of π participation seemed surprising since the **4S** compounds solvolyze by way of resonance-stabilized α-arylalkyl carbenium ions.[3] The involvement of the aliphatic double bond in the rate-determining step of the reactions of **4U** will tend to diminish the charge density at the reaction center and will thus reduce the effectiveness of the benzylic resonance stabilization of the transition state. Nevertheless, rate accelerations of up to a factor of 60 were observed. It seemed, therefore, appropriate to investigate the extent and the nature of the double bond involvement in more detail. Herewith we report the results of this investigation.

Results

Six series of compounds **1U**, **1S**, **2U**, **2S**, **3U**, and **3S** were prepared and their solvolysis rates measured. The results are shown in Tables I and II, together with previously reported rate constants for **4U** and **4S**.





1U, $R_1 = R_2 = H$ — **1S**, $R_1 = R_2 = H$
2U, $R_1 = CH_3$; $R_2 = H$ — **2S**, $R_1 = CH_3$; $R_2 = H$
3U, $R_1 = H$; $R_2 = CH_3$ — **3S**, $R_1 = H$; $R_2 = CH_3$
4U, $R_1 = R_2 = CH_3$ — **4S**, $R_1 = R_2 = CH_3$

a, Y = *p*-OCH_3; b, Y = *p*-CH_3; c, Y = H; d, Y = *p*-Br; e, Y = *m*-Br

Experimental Section

The chlorides 1–4 were prepared in 85–95% yields by reacting the corresponding carbinol with thionyl chloride in pyridine.[4] In all cases the NMR and IR spectra were consistent with the expected structure of the product. Parent carbinols were prepared from Grignard reagents of 1-bromoalkanes or 1-bromo-4-alkenes and substituted benzaldehydes. The yields were, after purification by either column (alumina) or liquid (Porosil, chloroform) chromatography, from 55–65%. All parent carbinols gave satisfactory elemental C and H analyses and expected NMR and IR spectra.

Solvolysis rates were followed by continuous titration of the liberated acid by means of a pH stat. Typically, 0.05 mmol of the substrate was dissolved in 25 mL of solvent thermostated to ±0.05 °C and liberated HCl titrated by using a 0.02 N solution of sodium alkoxide conjugate to the solvent. Each measurement was repeated at least once but usually 4–6 times. In all cases the first-order rate law was obeyed up to at least 80% reaction completion. Rate constants were calculated by using a nonlinear least-squares program.

Table I. Solvolysis of 1-Arylhexyl Chlorides and 1-Aryl-5-hexenyl Chlorides. Rate Constants for 1S and 1U

Y[b]	solvent[c]	T, °C	10^5k,[d] s^{-1} U[a]	10^5k,[d] s^{-1} S[a]	k_{1U}/k_{1S}
p-OCH_3	95E	5	142 (7)	289 (9)	0.49
p-CH_3		50	15.5 (8)	16.2 (7)	0.96
		60	49.1 (3)	49.1 (3)	1.00
	80E	25	8.92 (9)	8.57 (1)	1.04
		35	29.2 (1)	29.1 (8)	1.00
H		50	2.85 (7)	3.11 (29)	0.92
	97T	35	144 (6)	150 (3)	0.96
p-Br		30	18.7 (5)	16.2 (4)	1.15
m-Br		50	4.53 (14)	3.30 (11)	1.37
		60	11.4 (3)	8.63 (2)	1.32

[a] Aliphatic side chain (R); U unsaturated, S saturated. [b] Substituent on the phenyl ring. [c] 95E and 80E are 95 and 80 vol % aqueous ethanol, respectively, and 97T is 97 wt % aqueous 2,2,2-trifluoroethanol. [d] Numbers in parentheses are uncertainties of the last reported figure, i.e., 15.5 (8) = 15.5 ± 0.8; uncertainties are standard deviations of the mean.

Discussion

From the last column in Table I it can be seen that none of the compounds of series **1U** solvolyses much faster than the corresponding compound of the **1S** series. Thus the monosubstituted double bond of the aliphatic chain is not quite nucleophilic enough to act as an effective neighboring group. Analogously, in series **2**, **3**, and **4** all *p*-anisyl derivatives solvolyze practically at the same rate. Thus, if benzylic resonance stabilization of the transition state is

(1) (a) "Pliva" Pharmaceutical and Chemical Works. (b) Taken in part from the Ph.D. Thesis of I.M., University of Zagreb, 1976, and in part from the undergraduate research thesis of M.O., University of Zagreb, 1976. (c) Faculty of Pharmacy and Biochemistry.
(2) E. Polla, S. Borčić, and D. E. Sunko, *Tetrahedron Lett.*, 799 (1975).
(3) V. J. Shiner, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Am. Chem. Soc.*, **90**, 418 (1968).
(4) E. L. Eliel, M. T. Fish, and T. Prosser, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, 1963, p 169.

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Table II. Solvolysis of 1-Arylalkyl Chlorides and 1-Aryl-5-alkenyl Chlorides. Rate Constants

Y[a,d]	solvent[b]	T, °C	10^5k,[c] s^{-1} 2U	2S	3U	3S	4U	4S
p-OCH_3	95E	5	299 (4)	299 (3)	308 (4)	302 (2)	297 (1)	300 (1)
		10	537 (5)	527 (7)	522 (6)	530 (4)	536 (4)	529 (3)
		25	2765	2574	2285	2558	2800	2590
p-CH_3		60	47.4 (6)	46.3 (4)	58.5 (7)	51.4 (7)		
		50	19.7 (3)	17.4 (3)	24.3 (3)	17.5 (3)	34.9 (1)	17.5 (2)
		40					14.6 (2)	6.11 (1)
		25	1.70	1.13	2.09	0.86	3.54	1.10
	80E	25	13.2 (3)	11.7 (2)	17.5 (2)	12.2 (2)	28.1 (2)	12.6 (1)
H		60	11.5 (4)		29.3 (4)			
		50	5.16 (6)	3.45 (5)	12.8 (3)	3.55 (5)	22.6 (3)	3.98 (3)
		40		1.20 (2)		1.22 (3)	9.53 (5)	1.12 (1)
		25	0.550	0.214	1.27	0.214	2.34	0.145
	97T	25		42.9		47.1 (8)		51.5 (2)
p-Br	80E	60	3.93 (5)		6.54 (6)			
		50	1.55 (2)		2.75 (3)		6.38 (5)	
		40					2.20 (5)	
		25	0.115		0.245		0.389	
	97T	25	27.1 (3)	8.89 (9)	52.2 (7)	8.45 (9)	193 (1)	10.2 (1)
m-Br		50	11.3 (2)	2.56 (5)	17.6 (3)	2.65 (2)		2.91 (5)
		40	4.58 (4)	0.942 (8)	7.41 (9)	0.946 (8)		1.37 (2)
		25	1.06	0.185	1.82	0.177	23.4 (1)	0.402

[a] Substituent on the phenyl ring. [b] 95E and 80E are 95 and 80 vol % aqueous ethanol, respectively, 97T is 97 wt % aqueous 2,2,2-trifluoroethanol. [c] Numbers in parentheses are uncertainties of the last reported figure, i.e., 47.4 (6) = 47.4 ± 0.6; uncertainties are standard deviations of the mean. Rate constants reported without uncertainty are calculated values from other temperatures. [d] Satisfactory elemental C and H analyses (±0.3%) for all parent carbinols of the new compounds listed in the table were reported.

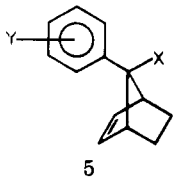
Table III. Relative Rates and Percent Participation in Solvolysis of Chlorides 2, 3, and 4 at 25 °C

Y	solvent	k_{2U}/k_{2S}	% participn[a]	k_{3U}/k_{3S}	% participn[a]	ratio[b]	product[c]	k_{4U}/k_{4S}	% participn[a]
p-OCH_3	95E	1.07	7	0.89	0	0.83	0.95	1.08	7
p-CH_3	95E	1.50	34	2.42	59	1.61	3.63	3.22	69
	80E	1.13	11	1.43	30	1.27	1.62	2.23	55
H	80E	2.57	61	5.93	83	2.30	15.2	16.1	94
p-Br	97T	3.05	67	6.18	84	2.03	18.9	18.9	95
m-Br	97T	5.73	83	10.3	90	1.80	59.0	58.2	98

[a] % participation = $100k_\Delta/k_t = 100(1 - k^S/k^U)$. [b] Value in column five divided by the corresponding value in column three. [c] Value in column three times the corresponding value in column five.

exalted by the electron-donating p-OCH_3 group, the anchimeric assistance of the aliphatic double bond becomes unimportant regardless of the degree or site of methyl substitution. In all other cases the compounds of the U series solvolyze faster than the corresponding compounds of the S series as can be seen from columns three, five, and nine of Table III. These accelerations appear to be significant and become important with electron-withdrawing groups.

A similar "leveling" of the neighboring-group participation has been observed in solvolysis of **5** by Gassman[5] who



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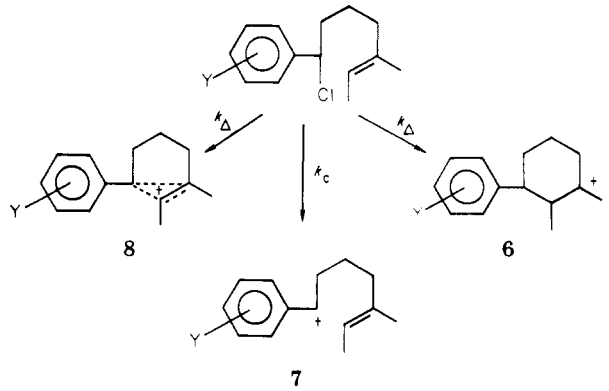
has also calculated the "leveling capacity" of the p-anisyl group. In an analogous manner it can be calculated that an unsubstituted phenyl group in **5** can overcome or "level" a neighboring-group participation responsible for a rate factor of 2.4×10^9. Provided that this number is not specific for **5** and can also be applied to double bond participation in general, then the fact that rate enhancements as reported in Table III can be observed at all is rather remarkable and indicative of the great tendency of the aliphatic bond at positions 5 to interact with a cationic center. In this respect it is illustrative to calculate the driving force for participation of the double bond in solvolysis **3U-c** from the rate ratio **3U-c/3S-c** (5.92 in 80% ethanol at 25 °C, Table III) and the above "leveling capacity" of the phenyl group. It amounts to about 14 kcal/mol [RT ln $(5.93 \times 2.4 \times 10^9)$]!

Carbonium vs. Carbenium Ions. Rate enhancements observed in reactions of **4U** could be interpreted as being due to transformation of a π to a σ bond, giving rise in the rate-determining step to a tertiary cyclohexyl cation **6**.



8 **6**

7

However, in **6** all of the benzylic resonance stabilization

(5) P. G. Gassman and A. F. Fentiman, Jr., *J. Am. Chem. Soc.*, **92**, 2549 (1970); **91**, 1545 (1969); P. G. Gassman, J. Zeller, and J. T. Lumb, *Chem. Commun.*, **69** (1968).

Table IV. Solvolysis of Chlorides 2, 3, and 4. Activation Parameters[a]

Y	sol-vent	2U $\Delta H^{\ddagger}$	2U $\Delta S^{\ddagger}$	2S $\Delta H^{\ddagger}$	2S $\Delta S^{\ddagger}$	$\Delta\Delta G^{\ddagger}$ (2U − 2S)	3U $\Delta H^{\ddagger}$	3U $\Delta S^{\ddagger}$	3S $\Delta H^{\ddagger}$	3S $\Delta S^{\ddagger}$	$\Delta\Delta G^{\ddagger}$ (3U − 3S)	4U $\Delta H^{\ddagger}$	4U $\Delta S^{\ddagger}$	4S $\Delta H^{\ddagger}$	4S $\Delta S^{\ddagger}$	$\Delta\Delta G^{\ddagger}$ (4U − 4S)
p-CH_3	95E	18.8	−19.5	20.9	−13.2	−0.2	18.8	−19.1	23.0	−6.7	−0.5	17.5	−22.3	21.1	−12.6	−0.7
H	80E	17.1	−27.4	21.2	−15.4	−0.5	17.7	−23.7	21.5	−14.5	−1.1	17.3	−23.7	25.5	−2.0	−1.6
m-Br	97T	18.1	−22.7	20.2	−19.5	−1.1	17.4	−24.0	20.7	−17.5	−1.4					

[a] $\Delta H^{\ddagger}$ and $\Delta\Delta G^{\ddagger}$ in kcal/mol, $\Delta S^{\ddagger}$ in cal/(deg mol), $\Delta\Delta G^{\ddagger}$ at 25 °C.

Table V. Free Energy Correlation in TFE at 25 °C

chlorides	n^a	ρ^+	r^b	s^c	ψ^d
2S	5	−6.24	0.998	0.22	0.082
2U	4	−4.83	0.998	0.11	0.089
	5	−5.60	0.996	0.32	0.115
3S	5	−6.40	0.998	0.23	0.082
3U	4	−4.67	0.993	0.20	0.167
	5	−5.66	0.991	0.39	0.173
4S	5	−6.31	0.997	0.25	0.100
4U	4	−3.94	0.998	0.10	0.089
	5	−4.83	0.992	0.31	0.163
1-arylethyl	8[e]	−6.09	0.998	0.23	0.068

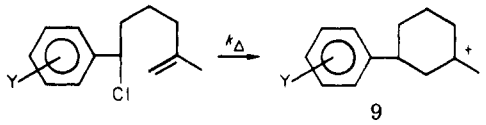
[a] Number of data points with ($n = 5$) or without ($n = 4$) the rate of the *p*-anisyl derivative. [b] Correlation coefficient. [c] Standard deviation of regression line. [d] Statistical test $\psi = [n(1 - r^2)/n - 2]^{1/2}$. A correlation is considered good if $\psi \leq 0.1$[18]. [e] Calculated from data in ref 3. Relative rates extrapolated from data in six different solvents.

inherent in the unassisted route producing **7** is lost. It is therefore possible that the double bond participation yields a charge-delocalized carbonium ion **8** rather than carbenium ion **6**. In **8** not all of the bonding energy due to $\pi \rightarrow \sigma$ bond transformation has been gained, but not all of the benzylic resonance stabilization has been lost. Such a compromise might make **8** more stable than **6**. The results of the present work indeed indicate a transition-state structure for participation resembling **8** rather than **6**.

An interesting feature of the results as presented in columns eight and nine of Table III is that the products of rate enhancements observed with **2U** (vs. **2S**) and **3U** (vs. **3S**) are very nearly equal to rate accelerations observed with **4U** (vs. **4S**). Such a methyl-group rate effect can be well understood in terms of charge-delocalized transition-state structures such as **8**. However, this cumulativity could only be apparent. Namely, it has been found convenient to analyze neighboring-group participation in terms of competing processes, the overall rate (k_t) being the sum of the rates of an unassisted ionization process (k_c) and of the neighboring-group process (k_Δ). Using the rate of the corresponding compound of the S series for k_c, we have calculated the contributions of k_Δ, and they are given in columns four, six, and ten of Table III (% participation = $100k_\Delta/k_t = 100(1 - k^S/k^U)$). It should be mentioned that, by analogy with the α-arylethyl[3] system, minor contributions of a third process, the nucleophilically solvent-assisted reactions (k_s), are possible in solvents with lower ionizing power and with substrates bearing electron-withdrawing substituents on the phenyl ring. In the present calculations this k_s component is included in the k_c value.

As pointed out by a referee, if the rates of unsaturated substrates are treated as the sum of two reactions (k_c and k_Δ), then it is not possible to ascertain from available data if the rate effects of methyl substitution are cumulative or not. Methyl substitution increases k_Δ, and in order to calculate the rate enhancements, k_Δ for the methyl-unsubstituted series (**1U**) should be known. However, **1U** reacts predominantly by way of k_c so that k_Δ values cannot be extracted from the data with an acceptable accuracy.

Another interesting feature of the results is that compounds of the **3U** series show rather larger rate enhancements than those of the **2U** series, as can be seen from columns three, five, and seven of Table III. It is difficult to rationalize this observation in terms of transition states resembling charge-localized carbenium ions. With **2U** a rate-determining cyclization would yield a tertiary carbenium ion **9** while with **3U** the analogous process could proceed only by way of secondary ions **10** and/or **11**. In



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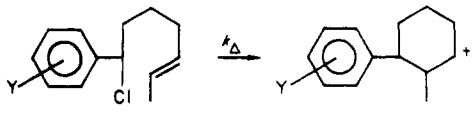

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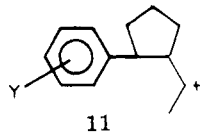

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view of the relative stabilities of these intermediates it could be expected that the driving force for participation would be significantly larger with **2U** than with **3U**, which is not the case. The relative reactivities of **2U** and **3U** are not easily explained even in terms of transition-state structures resembling charge-delocalized carbonium ions such as **8**. It is reasonable to expect that in **8** more positive charge would be delocalized to the more substituted end of the double bond which again leads to the wrong prediction that **2U** should be more reactive than **3U**. However, the expected difference in reactivities is much smaller for the latter mechanism than for the former. Thus, for example, in acid-catalyzed hydration, a reaction which proceeds by way of charge-localized carbenium ions, isobutene is about 10^4 times more reactive than *trans*-2-butene.[6-8] In bromination,[9] a reaction which proceeds by way of bridged bromonium ions, this reactivity ratio is only 3.

π Participation in solvolysis of the parent compound, 5-hexenyl *p*-nitrobenzenesulfonate (**12**), was investigated by Bartlett[10] and Trahanovsky.[11] The solvolysis of **12** is slightly enhanced relative to that of the *n*-hexyl derivative and yields significant amounts of cyclized products containing mostly cyclohexane derivatives. However, small

(6) Unpublished results of R. W. Taft, Jr.; see ref 7.
(7) T. H. Lowry and K. S. Richardson, "Mechanism and Theory in Organic Chemistry", Harper and Row, New York, 1976, p 339.
(8) See also P. D. Bartlett and G. D. Sargent, *J. Am. Chem. Soc.*, **87**, 1297 (1965).
(9) J. E. Dubois and G. Mouvier, *Bull. Soc. Chim. Fr.*, 1426 (1968); ref 7, p 350.
(10) P. D. Bartlett, W. D. Closson, and T. J. Cogdell, *J. Am. Chem. Soc.*, **87**, 1308 (1965); P. D. Bartlett, *Justus Liebigs Ann. Chem.*, **653**, 45 (1962).
(11) W. S. Trahanovsky and M. P. Doyle, *J. Am. Chem. Soc.*, **89**, 4867 (1967).

amounts (up to 4%) of cyclopentane derivatives[11] are also found consistently in conspicuous contrast to products of solvolysis of cyclohexyl *p*-nitrobenzenesulfonates.[12] The rationale is that π participation proceeds via a carbonium ion which can be attacked by solvent to yield products or to rearrange to a cyclohexyl cation. Since the attack of the nucleophile on the carbonium ion can occur at the unsubstituted carbon of the double bond, yielding cyclopentane derivatives, it follows that a significant amount of positive charge must be located at C_6 in the reaction intermediate. This is consistent with results reported in this work.

Activation Parameters. For reactions of compounds of the U series which show rate accelerations and where a comparison with the S series is possible from the available data, activation parameters were calculated. The calculated values are shown in Table IV. Although all activation parameters were calculated from rate data at two closely spaced temperatures and are therefore not very accurate, some trends are clearly apparent and probably significant. Thus, rate accelerations with the U series relative to S series (negative $\Delta\Delta G^{\ddagger}$) are in all cases due to a favorable enthalpy of activation which more than offsets a disfavorable entropy of activation. This is consistent with participation which lowers the enthalpy of activation through more extensive charge delocalization while increasing the entropy of activation by restricting the motions of the aliphatic side chain.

Linear Free-Energy Relationships. The rate constants for all three series of substrates with a saturated aliphatic side chain correlate well with σ^+ constants, as shown in Table V. This is rather remarkable since relative rates had to be extrapolated from data in three different solvents. Such a behavior seems general for the solvolysis of 1-arylalkyl chlorides. Thus, as shown in Table V, rate constants measured by Shiner[3] in solvolyses of 1-arylethyl chlorides correlate very well with σ^+ constants. The relative rates were extrapolated from data in six different solvents and encompass a range of 10^{10}. Also, the ρ^+ value obtained from Shiner's data is essentially the same[13] as those for **2S**, **3S**, and **4S**. The applicability of the $\rho^+\sigma^+$ correlation indicates that in these series ρ^+ values are not very solvent dependent and that in none of the cases does the direct displacement by the solvent (k_s) represent a major reaction pathway.

Using the same extrapolation procedure, we obtained a good fit for the **4U** series if the point for the *p*-anisyl derivative is excluded. The correlation is worse if the latter point is included, which is illustrated in Figure 1. In solvolysis of **5** it has been shown that the ρ^+ value changes at the point where the reaction mechanism changes from predominantly k_Δ to predominantly k_c. The plots in Figure 1 suggest a similar breakdown of the $\rho^+\sigma^+$ correlation with the *p*-anisyl derivative. This is consistent with results presented in Table III since double bond participation seems to be the major reaction pathway for all compounds of the **4U** series except for the *p*-anisyl derivative.

There is much less of an indication of change in mechanism in the free-energy correlations obtained from the data with **2U** and especially with **3U**. This, however, is not surprising since with these series the change in mechanism is more gradual so that most compounds react with significant contributions of both k_Δ and k_c (Table III). All

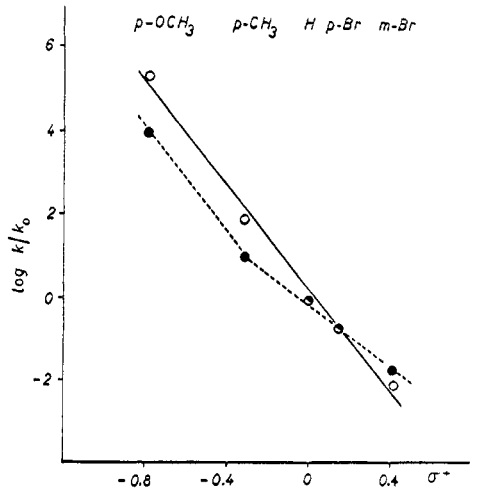
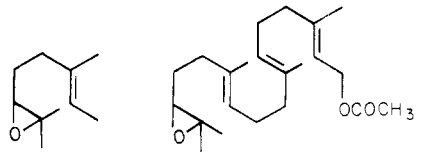


Figure 1. $\rho^+\sigma^+$ plot for trifluoroethanolysis (25 °C) of 1-aryl-5-methyl-5-heptenyl chlorides (●) and 1-aryl-5-methylheptyl chlorides (○). The half-solid circles represent values for both of these groups.

parameters relevant to free-energy correlations are given in Table V.

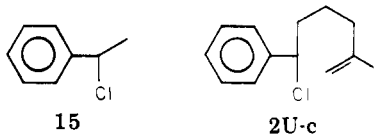
Finally, the large negative ρ^+ value calculated for the k_Δ process in the reactions of **4U** (Table V) must be due to considerable benzylic resonance stabilization of the transition states, which is consistent with structure **8** but not **6**.

Olefinic Polycyclizations. Since the results of this work might be relevant to the elucidation of the mechanism of biomimetic olefinic polycyclizations,[14,15] a final remark seems appropriate. van Tamelen[16] has shown that acid-catalyzed epoxide ring opening in **13** occurs with



13 **14**

participation of the double bond. In an attempt to detect participation of additional π bonds in systems of the type where polycyclization is extensive, the rate of disappearance of epoxide **13** was compared inter alia with that of **14**. A rate ratio of **13**/**14** of 1.3 ± 0.2 was found which was used as an argument against a polycyclization mechanism involving participation of additional double bonds in **14**. This argument rests on the assumption that **13** is an adequate reference compound for detecting participation with **14** which, in our opinion, is not the case. Thus, **15** could



15 **2U-c**

have been used as a reference for detecting participation with **2U-c** with as much justification as **13** for detecting additional participation with **14**.

The rates in 80% ethanol at 25 °C are[3] $k = 1.00 \times 10^{-5}$ s^{-1} for **15** and 0.55×10^{-5} s^{-1} for **2U-c**, giving a rate ratio of **15**/**2U-c** of 1.82. Hence, the conclusion could have been reached that **2U-c** solvolyzes without anchimeric assistance

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(13) T. G. Traylor and J. C. Ware, *J. Am. Chem. Soc.*, **89**, 2304 (1967), report for solvolysis of 1-arylethyl chlorides in 95% aqueous ethanol at 25 °C a ρ^+ of −6.1 which is identical with the value obtained from data in ref 3.
(14) W. S. Johnson, *Acc. Chem. Res.*, **1**, 1 (1968).
(15) E. E. van Tamelen, *Acc. Chem. Res.*, **1**, 111 (1968).
(16) E. E. van Tamelen and D. R. James, *J. Am. Chem. Soc.*, **99**, 950 (1977).

of the double bond. Yet, when a more realistic standard is used for estimating k_c, it appears that over half of the reaction proceeds by way of participation (Table III)! Since small rate enhancements can conceal considerable participation, the choice of the reference substrate must be made with utmost care.

Extended π participation, if operative, might be quite elusive to detection by kinetic means. Thus even if all of the 20% of tricyclic products obtained in the reaction of **14** were to arise by this mechanism, the resultant rate enhancement would be only a factor 1.25. Moreover, this calculation rests on the assumption that all other competitive processes proceed at exactly the same rate in reactions both of **14** and of the reference epoxide. Therefore, both the choice of substrates and the experimental method used by van Tamelen are too crude and inadequate for detecting extended π participation.

In view of the above consideration it is remarkable that extended π participation has nevertheless successfully been demonstrated in a Lewis acid catalyzed polycyclization of allylic alcohols.[17]

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

Registry No. **1U** (Y = *p*-OCH_3), 71434-63-4; **1U** (Y = *p*-CH_3), 71434-64-5; **1U** (Y = H), 61608-88-6; **1U** (Y = *p*-Br), 71434-65-6; **1U** (Y = *m*-Br), 71434-66-7; **1S** (Y = *p*-OCH_3), 71434-02-1; **1S** (Y = *p*-CH_3), 71434-67-8; **1S** (Y = H), 71434-68-9; **1S** (Y = *p*-Br), 71434-69-0; **1S** (Y = *m*-Br), 71434-70-3; **2U** (Y = *p*-OCH_3), 71434-71-4; **2U** (Y = *p*-CH_3), 71434-72-5; **2U** (Y = H), 71434-73-6; **2U** (Y = *p*-Br), 71434-74-7; **2U** (Y = *m*-Br), 71434-75-8; **2S** (Y = *p*-OCH_3), 71434-76-9; **2S** (Y = *p*-CH_3), 71434-77-0; **2S** (Y = H), 71434-78-1; **2S** (Y = *p*-Br), 71434-79-2; **2S** (Y = *m*-Br), 71434-80-5; **3U** (Y = *p*-OCH_3), 71434-81-6; **3U** (Y = *p*-CH_3), 71434-82-7; **3U** (Y = H), 71434-83-8; **3U** (Y = *p*-Br), 71486-21-0; **3U** (Y = *m*-Br), 71434-84-9; **3S** (Y = *p*-OCH_3), 71434-45-2; **3S** (Y = *p*-CH_3), 71434-46-3; **3S** (Y = H), 71434-47-4; **3S** (Y = *p*-Br), 71434-48-5; **3S** (Y = *m*-Br), 71434-49-6; **4U** (Y = *p*-OCH_3), 71434-50-9; **4U** (Y = *p*-CH_3), 71434-51-0; **4U** (Y = H), 71434-52-1; **4U** (Y = *p*-Br), 71434-53-2; **4U** (Y = *m*-Br), 71434-54-3; **4S** (Y = *p*-OCH_3), 56040-07-4; **4S** (Y = *p*-CH_3), 56040-08-5; **4S** (Y = H), 56040-10-9; **4S** (Y = *p*-Br), 56040-09-6; **4S** (Y = *m*-Br), 56040-11-0; 1-bromopentane, 110-53-2; 1-bromo-4-methylpentane, 626-88-0; 1-bromohexane, 111-25-1; 1-bromo-4-methylhexane, 71434-55-4; 1-bromo-4-pentene, 1119-51-3; 1-bromo-4-methylpent-4-ene, 41182-50-7; 1-bromo-4-hexene, 36851-77-1; 1-bromo-4-methylhex-4-ene, 30316-02-0; *p*-methoxybenzaldehyde, 123-11-5; *p*-methylbenzaldehyde, 104-87-0; benzaldehyde, 100-52-7; *p*-bromobenzaldehyde, 1122-91-4; *m*-bromobenzaldehyde, 3132-99-8; α-(4-pentenyl)-4-methoxybenzyl alcohol, 71434-56-5; α-(4-pentenyl)-4-methylbenzyl alcohol, 71434-57-6; α-(4-pentenyl)benzyl alcohol, 65727-70-0; α-(4-pentenyl)-4-bromobenzyl alcohol, 71434-58-7; α-(4-pentenyl)-3-bromobenzyl alcohol, 71434-59-8; 1-(*p*-methoxyphenyl)hexanol, 71434-60-1; 1-(*p*-methylphenyl)hexanol, 71434-61-2; 1-phenylhexanol, 4471-05-0; 1-(*p*-bromophenyl)hexanol, 71434-62-3; 1-(*m*-bromophenyl)hexanol, 71434-16-7; α-(4-methyl-4-pentenyl)-4-methoxybenzyl alcohol, 71434-17-8; α-(4-methyl-4-pentenyl)-4-methylbenzyl alcohol, 71434-18-9; α-(4-methyl-4-pentenyl)benzyl alcohol, 71434-19-0; α-(4-methyl-4-pentenyl)-4-bromobenzyl alcohol, 71434-20-3; α-(4-methyl-4-pentenyl)-3-bromobenzyl alcohol, 71434-21-4; 1-(*p*-methoxyphenyl)-5-methylhexanol, 71434-22-5; 1-(*p*-methylphenyl)-5-methylhexanol, 71434-23-6; 1-phenyl-5-methylhexanol, 37563-31-8; 1-(*p*-bromophenyl)-5-methylhexanol, 71434-24-7; 1-(*m*-bromophenyl)-5-methylhexanol, 71434-25-8; α-(4-hexenyl)-4-methoxybenzyl alcohol, 71434-26-9; α-(4-hexenyl)-4-methylbenzyl alcohol, 71434-27-0; α-(4-hexenyl)benzyl alcohol, 71434-28-1; α-(4-hexenyl)-4-bromobenzyl alcohol, 71434-29-2; α-(4-hexenyl)-3-bromobenzyl alcohol, 71434-30-5; 1-(*p*-methoxyphenyl)heptanol, 71434-31-6; 1-(*p*-methylphenyl)heptanol, 71434-32-7; 1-phenylheptanol, 614-54-0; 1-(*p*-bromophenyl)heptanol, 71434-33-8; 1-(*m*-bromophenyl)heptanol, 71434-34-9; α-(4-methyl-4-hexenyl)-4-methoxybenzyl alcohol, 71434-35-0; α-(4-methyl-4-hexenyl)-4-methylbenzyl alcohol, 71434-36-1; α-(4-methyl-4-hexenyl)benzyl alcohol, 71434-37-2; α-(4-methyl-4-hexenyl)-4-bromobenzyl alcohol, 71434-38-3; α-(4-methyl-4-hexenyl)-3-bromobenzyl alcohol, 71434-39-4; 1-(*p*-methoxyphenyl)-5-methylheptanol, 71434-40-7; 1-(*p*-methylphenyl)-5-methylheptanol, 71434-41-8; 1-phenyl-5-methylheptanol, 71434-42-9; 1-(*p*-bromophenyl)-5-methylheptanol, 71434-43-0; 1-(*m*-bromophenyl)-5-methylheptanol, 71434-44-1.

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