A Case of Extended π-Participation. Solvolysis Rate of 1-Phenyl-5,9-dimethylundeca-5,9-dienyl Chloride

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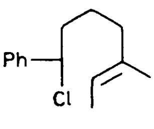
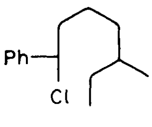
The title compound (**2**) solvolyses nine times faster than 1-phenyl-5-methylhept-5-enyl chloride (**1U**) owing to participation of both aliphatic double bonds.

Although much synthetic work using biomimetic cationic olefinic polycyclizations has been reported,[1] the mechanism of these reactions is not well understood; it is not certain whether two or more rings are formed in a concerted manner or whether the polycyclization is a step-wise process proceeding through one or more partially cyclized intermediates.[2,3] There are few examples where either the concerted[4] or the step-wise nature[3] of these reactions has been unequivocally demonstrated. We now report pertinent kinetic measurements.

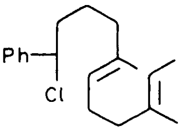
We have already reported on the solvolysis of (**1U**) and related chlorides.[5] Comparison (rate enhancements, methyl-substituent rate effects, secondary α-, β-, and ω-deuterium isotope effects, $\rho\sigma$-correlations, and activation parameters) of the reactivities of (**1U**) and the saturated analogue (**1S**) showed that (**1U**) reacts with anchimeric assistance. Here, nucleophilic participation by the aliphatic double bond (π-participation) leading to a bridged carbonium ion (k_{Δ}^{1}) competes efficiently with the formation of a secondary benzyl cation (k_{C}). This provides a basis for detecting and investigating possible extended π-participation (k_{Δ}^{2}) in the solvolysis of (**2**). It was expected that the involvement of the terminal double bond in the rate determining step would result in an increased solvolytic reactivity of (**2**) relative to (**1U**).



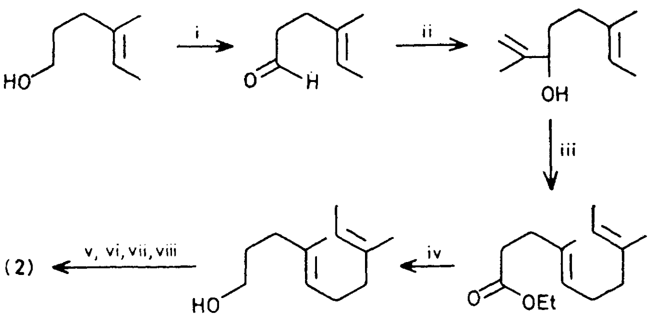
(1U)



(1S)



(2)



Scheme 1. *Reagents:* i, pyridine-HCl, CrO_3; ii, $CH_2{=}C(Me)MgBr$; iii, $MeC(OEt)_3$, $MeCH_2CO_2H$; iv, $LiAlH_4$; v, PBr_3; vi, Mg–Et_2O; vii, PhCHO; viii, $SOCl_2$.

The chloride (**2**)† was prepared by the reactions in Scheme 1 and solvolysed in ethanol–water (80:20 v/v). Rates were measured by continuous titration of the liberated acid by a pH-stat.

The calculated first order rate constants are ($\times 10^{-4}\ s^{-1}$): 3.61 ± 0.14 (35 °C), 7.40 ± 0.06 (50 °C), and 13.8 ± 0.5 (65 °C).‡ In Table 1 the reaction rates and activation parameters of the chlorides (**1S**), (**1U**), and (**2**) are compared. At 25 °C (**2**) reacts about nine times faster than (**1U**). This might not seem an impressive rate enhancement. However, if this acceleration is due to extended π-participation then a simple calculation§ shows that at least 89% of the products are formed by way of k_{Δ}^{2}.

Table 1. Relative solvolysis rates in ethanol–water (80:20 v/v) at 25 °C and activation parameters.

Chloride	k_{rel}	$\Delta H^{\ddagger}$ /kJ mol^{-1}	$-\Delta S^{\ddagger}$ /J K^{-1} mol^{-1}
(**1S**)	1	107.6 ± 2.5	3.8 ± 7.8
(**1U**)	16	73.2 ± 3.4	88.1 ± 10.7
(**2**)	144	35.9 ± 3.8	194.4 ± 11.7

It is believed that this is indeed the case for the following reasons. (a) Lengthening of the aliphatic side chain decreases k_{c} [1-phenylethyl chloride solvolyses 7 times faster than (**1S**) under the conditions given in Table 1][5a] and possibly k_{Δ}^{1} as well; (b) the inductive effect of the double bonds would be expected, if anything, to decrease k_{c} and k_{Δ}^{1}; (c) the whole rate acceleration of (**2**) relative to (**1U**) is due to a large change in $\Delta H^{\ddagger}$ overcompensating a very unfavourable change in $\Delta S^{\ddagger}$. This is quite consistent with extended π-participation since a high degree of order is required in the transition state of this reaction relative to the ground state.[6] Qualitatively, the same trend is observed with (**1U**) relative to (**1S**). To our knowledge, there is no other solvolysis reaction with such a low $\Delta H^{\ddagger}$ as that of (**2**) whose rate can be followed at conventional temperatures and by conventional methods.

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† The carbinol precursor of chloride (**2**) gave a ^1H n.m.r. spectrum consistent with its structure.

‡ Uncertainties are standard deviations of the mean. Solvolyses followed the first order rate law at least up to 80% completion.

§ The titrimetric rate constant $k_{\mathrm{t}} = k_{\mathrm{c}} + k_{\Delta}^{1} + k_{\Delta}^{2}$. The rate of (**1U**) $\geqslant k_{\mathrm{c}} + k_{\Delta}^{1}$ (see further discussion). Using relative rates then $9 \leqslant 1 + k_{\Delta}^{2}$ or $k_{\Delta}^{2} \geqslant 8$. The fraction of products formed by way of k_{Δ}^{2} should be equal to $k_{\Delta}^{2}/k_{\mathrm{t}}$ which is equal to at least 8/9 or 89%.

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