

Lack of Secondary β -Deuterium Kinetic Isotope Effect in the Solvolysis of 2-Chloro-2,6,10-trimethyldodeca-6,10-diene. Indication of Extended Π -Participation

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The title compound (**3**) with two deuteriated methyl groups attached to the reaction centre undergoes solvolysis without a kinetic isotope effect indicating participation of both double bonds.

The epoxide related to the protio analogue of (**3**) (2,3-epoxy-2,6,10-trimethyldodeca-6,10-diene) reacts with extensive bicyclization upon Lewis acid epoxide ring opening but without rate acceleration due to the presence of the second double bond (*i.e.* relative to 2,3-epoxy-2,6-dimethyloct-6-ene).¹

A series of chlorides related to (**2**) all undergo solvolysis with small or no rate acceleration relative to their saturated analogues.^{2,3} However, significantly reduced secondary β -deuterium kinetic isotope effects (*k.i.e.*) indicate a delocalization of the positive charge away from the reaction centre in the transition state due to participation of the double bond.³

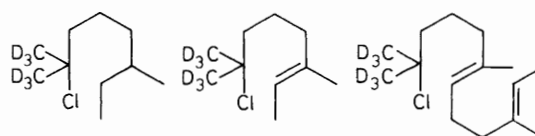
In order to test for possible extended Π -participation, (**3**) and its protio analogue were prepared by the published scheme⁴ using, in the penultimate step, deuterioacetone and acetone, respectively instead of benzaldehyde. The results of solvolysis rate measurements are given below (80% v/v EtOH at 50 °C).

The magnitude of secondary β -deuterium *k.i.e.* are the most sensitive indication of charge dispersal and thus of neighbouring group participation. Many examples are given elsewhere.³ In contrast, rate acceleration (in our case k_U = rate of the unsaturated chloride, k_S = rate of the saturated chloride) is indicative of participation only if k_U/k_S is large. However, a small k_U/k_S does not prove lack of participation.^{2,5}

The results given above can be rationalized in the following manner. 1. The saturated chloride (**1**) undergoes solvolysis with the expected secondary β -deuterium *k.i.e.*⁶ 2. The unsaturated chloride (**2**) undergoes solvolysis with a moderate rate acceleration but a significantly reduced secondary β -deuterium *k.i.e.* indicating the participation of the double bond.³ 3. The doubly unsaturated chloride (**3**) undergoes solvolysis without a rate acceleration but the lack of secondary β -deuterium *k.i.e.* may indicate participation of both double bonds.[†]

The decreasing trend in *k.i.e.* from (**1**) to (**2**) to (**3**) is interpreted as being due to an increasing charge delocalization from the reaction centre of the transition states in the series.

Previously,⁴ we have measured the solvolysis rate of the benzylic analogue of (**3**) (1-chloro-5,9-dimethyl-1-phenylundeca-5,9-diene). Only a moderate rate increase ($k_U/k_S = 144$) was found but activation parameters are in accord with a mechanism involving participation of both double bonds. The



	(1)	(2)	(3)
k_U/k_S	—	19	1.1
k_H/k_D	1.80 ± 0.03	1.37 ± 0.03	1.01 ± 0.04

rate effect is due to the lowering of the ΔH^\ddagger which overcompensates a large (negative) ΔS^\ddagger . Extensive charge delocalization is expected to reduce ΔH^\ddagger . On the other hand the high degree of order required in the transition state of the substrate reacting by way of participation of both double bonds should be responsible for an unfavourable ΔS^\ddagger . A similar trend is also observed in solvolysis of (**3**) relative to the saturated analogue ($\Delta H^\ddagger = 64$ vs. 90 kJ mol⁻¹ and $\Delta S^\ddagger = -118$ vs. -37 J mol⁻¹ K⁻¹) and is interpreted in a same manner.

Acknowledgements

We are grateful for financial support to the Yugoslav-American Board for Scientific and Technological Cooperation (Research Council of Croatia and National Science Foundation). We thank V. J. Shiner, Jr. from Indiana University for very useful discussions.

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Received 10th January 1989

(Accepted 10th May 1989); Paper 9/01959F

[†] The fact that (CD₃)₂CClCH₂CH₃ undergoes solvolysis with the same *k.i.e.* as (**1**) can be taken as evidence that the lack of *k.i.e.* with (**3**) is not due to some 'mass effect'.