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Malnar, Ivica; Kronja, Olga; Humski, Krešimir; Borčić, Stanko

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Preliminary Communication

Solvolysis Kinetics of 1-Chloro-1-phenyl- -5,9,14,18,22-pentamethyl-5,9,13,17,21-tricosapentaene, a Squalene Derivative. Indication of Participation*

Ivica Malnar, Olga Kronja, Krešimir Humski, and Stanko Borčić

*Faculty of Pharmacy and Biochemistry, University of Zagreb, A. Kovačića 1, 41000
Zagreb, Croatia*

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The title compound **1** was prepared starting from squalene and the solvolysis rates were measured in 80% (v/v) aqueous ethanol. The relative solvolysis rate and activation parameters were calculated. According to the values obtained it is concluded that **1** solvolyzes probably with participation of at least one double bond.

The precursor to steroid hormones and triterpenes in nature seems to be 2,3-epoxysqualene.¹ The latter compound upon biomimetic acid catalyzed epoxide ring opening yields tricyclic products.² In our effort to clarify the mechanism of biomimetic (poly)cyclizations,^{1a,b,3} an investigation which has been initiated in collaboration with Sunko,⁴ we have recently prepared the title compound **1** according to the Scheme.

The chloride **1** was solvolyzed and rate constants measured at different temperatures. The results are given in Table I. In Table II the results obtained are compared with those previously published.^{4a,5}

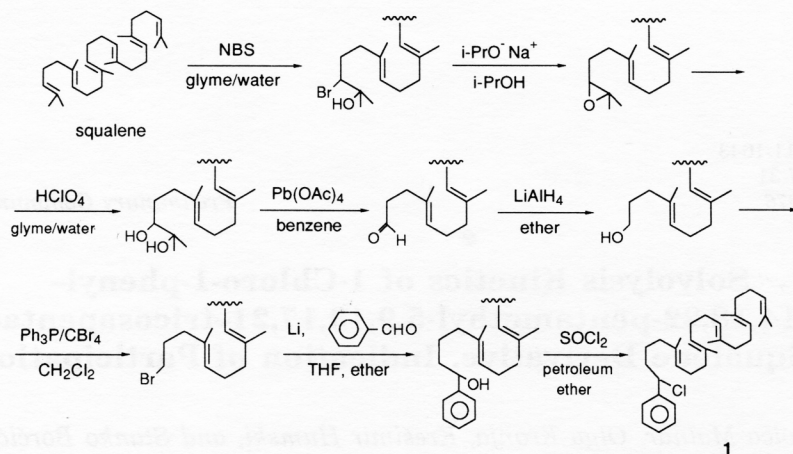
TABLE I

Solvolysis rate constants, relative solvolysis rate and activation parameters of 1-chloro-1-phenyl-5,9,14,18,22-pentamethyl-5,9,13,17,21-tricosapentaene in 80% (v/v) aqueous ethanol

<i>t</i> /°C	<i>k</i> /10 ⁻⁴ s ⁻¹ ^a	<i>k</i> _U / <i>k</i> _S ^c	$\frac{\Delta H^\ddagger}{\text{kJ mol}^{-1}}$	$\frac{-\Delta S^\ddagger}{\text{J K}^{-1} \text{ mol}^{-1}}$
70	5.39 ± 0.06			
60	2.30 ± 0.04			
50	1.23 ± 0.02			
25	0.142 ^b	15.8 ^d	65 ± 7 ^e	119 ± 21 ^e

^a Uncertainties are standard errors; ^b Extrapolated value; ^c Rate of unsaturated *vs.* the corresponding chloride with the saturated side chain; ^d Extrapolated value, Ref. 4c; ^e Uncertainties are standard deviations.

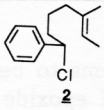
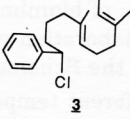
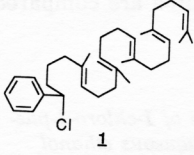
* Dedicated to Professor Dionis E. Sunko on the occasion of his seventieth birthday



Scheme

TABLE II

Solvolysis rate constants at 25 °C, relative solvolysis rates and activation parameters of some 1-phenylalk-5-enyl chlorides in 80% (v/v) aqueous ethanol

Compound	k/s^{-1} ^a	k_U/k_S ^c	$\frac{\Delta H^\ddagger}{kJ\ mol^{-1}}$	$\frac{-\Delta S^\ddagger}{J\ K^{-1}\ mol^{-1}}$	Ref.
 2	2.34×10^{-5} (1.45×10^{-6}) ^b	16.1	72.3 (104 ± 6) ^{b,d}	99.0 (9 ± 21) ^{b,d}	4a,b 4a,b,c
 3	2.24×10^{-4} (1.44×10^{-6}) ^b	155.6	36 ± 4 (104 ± 1) ^{b,d}	194 ± 12 (9 ± 2) ^{b,d}	4d 4c
 1	1.42×10^{-5} (9.0×10^{-7}) ^b	15.8	65 ± 7	119 ± 21	4c

^a Extrapolated values; ^b Data for analogues with the saturated side chain are shown in parentheses; ^c Rate of unsaturated *vs.* the corresponding chloride with the saturated side chain; ^d Uncertainties are standard deviations

The rate acceleration of **1** is relatively small compared to the analogue with the saturated side chain. However, the rate increase is comparable to that of chloride **2** for which participation has been shown to occur.^{4a,5a,b}

Moreover, the activation parameters (low enthalpy and high negative entropy of activation) akin to those of the doubly unsaturated chloride **3** are also indicative of participation. We conclude that the title compound **1** solvolyses in 80% (*v/v*) aqueous ethanol with participation of at least one double bond.

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SAŽETAK

Solvoliza 1-fenil-1-klor-5,9,14,18,22-pentametil-5,9,13,17,21-trikosapentaena, derivata skvalena. Indikacija participacije

Ivica Malnar, Olga Kronja, Krešimir Humski i Stanko Borčić

Polazeći od skvalena pripremljen je spoj **1** (1-fenil-1-klor-5,9,14,18,22-pentametil-5,9,13,17,21-trikosapentaen), te su izmjerene konstante brzina njegove solvolize u 80% (v/v) vodenom etanolu. Izračunana je relativna brzine solvolize i aktivacijski parametri. Iz dobivenih podataka slijedi da spoj **1** vjerojatno solvolizira uz participaciju barem jedne dvostruke veze.