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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*

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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]

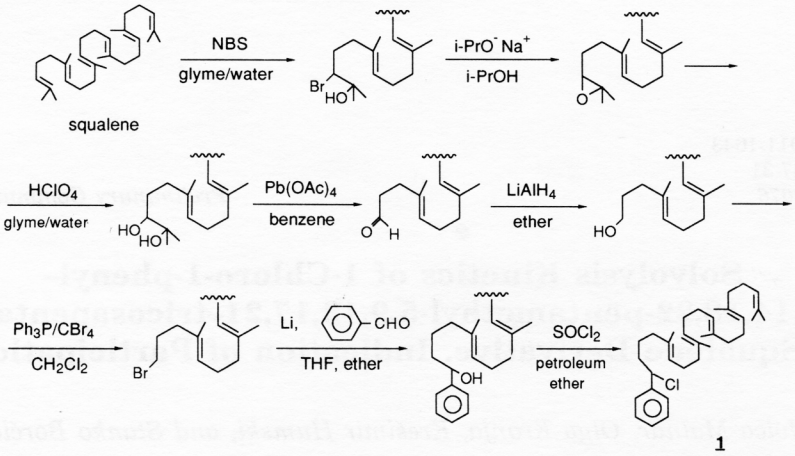
TABLE I

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

t/°C	$k/10^{-4}s^{-1}$ [a]	k_U/k_S [c]	$\frac{\Delta H^{\neq}}{kJ\ mol^{-1}}$	$\frac{-\Delta S^{\neq}}{J\ K^{-1}\ mol^{-1}}$
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.

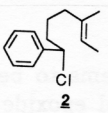
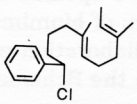
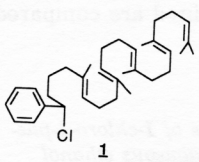
* Dedicated to Professor Dionis E. Sunko on the occasion of his seventieth birthday



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]	$\Delta H^{\neq}$ / kJ mol^{-1}	$-\Delta S^{\neq}$ / 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

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Polazeći od skvalena pripravljen 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.