

# 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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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.<sup>1</sup> The latter compound upon biomimetic acid catalyzed epoxide ring opening yields tricyclic products.<sup>2</sup> In our effort to clarify the mechanism of biomimetic (poly)cyclizations,<sup>1a,b,3</sup> an investigation which has been initiated in collaboration with Sunko,<sup>4</sup> 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.<sup>4a,5</sup>

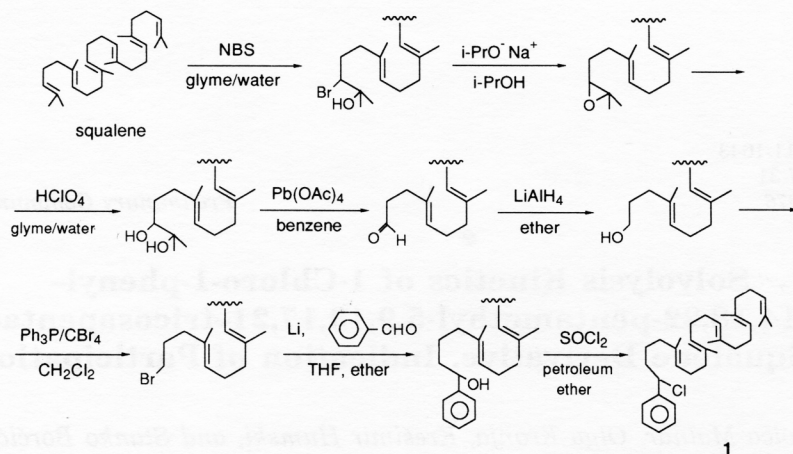
TABLE I

*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 <sup>-4</sup> s <sup>-1</sup> <sup>a</sup> | <i>k</i> <sub>U</sub> / <i>k</i> <sub>S</sub> <sup>c</sup> | $\frac{\Delta H^\ddagger}{\text{kJ mol}^{-1}}$ | $\frac{-\Delta S^\ddagger}{\text{J K}^{-1} \text{ mol}^{-1}}$ |
|--------------|---|--|--|---|
| 70           | 5.39 ± 0.06   |  |  |   |
| 60           | 2.30 ± 0.04   |  |  |   |
| 50           | 1.23 ± 0.02   |  |  |   |
| 25           | 0.142 <sup>b</sup>                                      | 15.8 <sup>d</sup>  | 65 ± 7 <sup>e</sup>                            | 119 ± 21 <sup>e</sup>   |

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

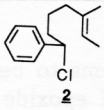
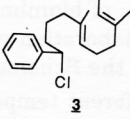
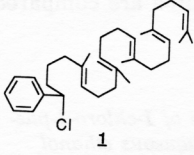
\* Dedicated to Professor Dionis E. Sunko on the occasion of his seventieth birthday



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

<sup>a</sup> Extrapolated values; <sup>b</sup> Data for analogues with the saturated side chain are shown in parentheses; <sup>c</sup> Rate of unsaturated *vs.* the corresponding chloride with the saturated side chain; <sup>d</sup> 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.<sup>4a,5a,b</sup>

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.