

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

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

Source / Izvornik: **Croatica Chemica Acta, 1992, 65, 547 - 549**

Journal article, Published version

Rad u časopisu, Objavljena verzija rada (izdavačev PDF)

Permanent link / Trajna poveznica: <https://urn.nsk.hr/urn:nbn:hr:163:698487>

Rights / Prava: [In copyright/Zaštićeno autorskim pravom.](#)

Download date / Datum preuzimanja: **2024-05-12**



Repository / Repozitorij:

[Repository of Faculty of Pharmacy and Biochemistry University of Zagreb](#)



ISSN 0011-1643
 UDC 547.31
 CCA—2076

Preliminary Communication

Solvolytic 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

Received March 26, 1992

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}

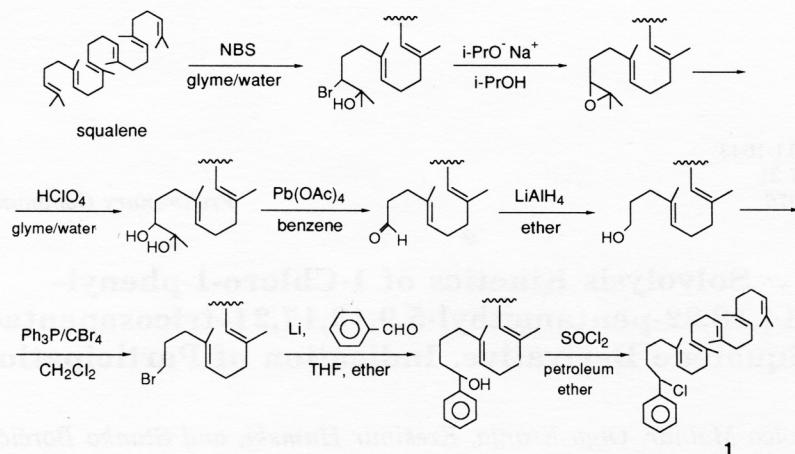
TABLE I

*Solvolytic 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_U</i> / <i>k_S</i> ^c	$\frac{\Delta H^{\ddagger}}{kJ \ mol^{-1}}$	$\frac{-\Delta S^{\ddagger}}{J \ K^{-1} \ mol^{-1}}$
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	$\frac{\Delta H^\ddagger}{kJ mol^{-1}}$	$\frac{-\Delta S^\ddagger}{J K^{-1} mol^{-1}}$	Ref.
	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
	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
	1.42×10^{-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.

Acknowledgement. – We are grateful to National Science Foundation (Grant 825) for partial financial support of this research

REFERENCES

1. (a) E. E. van Tamelen, *Acc. Chem. Res.* **1** (1968) 111; (b) **8** (1975) 152; (c) L. J. Mulheirn and P. J. Ramm, *Chem. Soc. Rev.* **1** (1972) 259; (d) E. E. van Tamelen, A. D. Pedlar, E. Li, and D. R. James, *J. Amer. Chem. Soc.* **99** (1977) 6778.
2. (a) E. E. van Tamelen, J. Willet, M. Schwartz, and R. Nadeau, *J. Amer. Chem. Soc.* **88** (1966) 5937; (b) E. E. van Tamelen and D. R. James, *J. Amer. Chem. Soc.* **99** (1977) 950.
3. (a) W. S. Johnson, *Acc. Chem. Res.* **1** (1968) 1; (b) *Angew. Chem. Int. Ed. Eng.* **15** (1976) 9; (c) *Bioorg. Chem.* **5** (1976) 51; (d) E. E. van Tamelen, *J. Amer. Chem. Soc.* **104** (1982) 6480; (e) O. Kronja, S. Borčić, K. Humski, and C. S. Foote, *Croat. Chem. Acta* **63** (1990) 193; (f) O. Kronja, M. Orlović, K. Humski, and S. Borčić, *J. Amer. Chem. Soc.* **113** (1991) 2306; (g) M. Orlović, S. Borčić, K. Humski, O. Kronja, V. Imper, E. Polla, and V. J. Shiner, *J. Org. Chem.* **56** (1991) 1874.
4. (a) E. Polla, S. Borčić, and D. E. Sunko, *Tetrahedron Lett.* (1975) 799; (b) I. Mihel, J. Šistek, S. Borčić, K. Humski, and D. E. Sunko, *J. Org. Chem.* **44** (1979) 4091; (c) E. Polla, S. Borčić, and D. E. Sunko, *J. Org. Chem.* **44** (1979) 4096.
5. (a) I. Mihel, M. Orlović, E. Polla, and S. Borčić, *J. Org. Chem.* **44** (1979) 4086; (b) M. Orlović, O. Kronja, K. Humski, S. Borčić, and E. Polla, *J. Org. Chem.* **51** (1986) 3253; (c) O. Kronja, E. Polla, and S. Borčić, *J. Chem. Soc., Chem. Commun.* (1983) 1044.

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 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.