Tetrahedron Letters,Vol.23,No.4,pp 463-464,1982 0040-4039/82/040463-02$03.00/0
Printed in Great Britain

5-CYCLOPENTYL-5-HYDROXYPENTANOIC AND 4-(2'-HYDROXYCYCLOHEXYL)-BUTANOIC ACIDS LACTONES OBTENTION BY ANODIC OXIDATION OF 1-DECALONE

Fructuoso Barba*, Antonio Guirado, Isidoro Barba and Marcelo Lopez
Department of Organic Chemistry, Faculty of Sciencie
University of Murcia, Spain

The 1-decalone anodic oxidation products in alkaline hydroalcoholic medium with platinum anode are identified. The 5-cyclopentyl-5-hydroxypentanoic acid lactone formation evidence a ring contraction process through a carbocationic intermediate.

The electrolysis of 1-decalone solutions in EtOH-Na_2CO_3 aq. 0,1 M in 1:1 ratio, carried out under constant current intensity conditions, with platinum anode and cathode in an undivided cell, gave two reaction products, 4 and 5. 5 was the major product. GC-MS analysis showed for both products the same molecular weigth, but different fragmentation paths; 4 m/e (relative intensity) 168 $M^{+\cdot}$ (10), 150(6), 84(88), 67(40), 55(50), 42(76), 41(100), 39(78); 5 m/e (relative intensity) 168 $M^{+\cdot}$ (8), 150(13), 140(12), 99(58), 71(46), 70(23), 69(31), 67(35), 55(38), 43(50), 42(69), 41(100), 39(69). The reaction products 4 and 5, were separated and purified by TLC. IR spectra of both compounds showed strong absortion in the carbonyl region, the 4 compound at 1728 cm^{-1} and the 5 compound at 1735 cm^{-1}.

The spectral data of 5 are in accordance with the δ lactonic structure of the 5-cyclopentyl-5-hydroxypentanoic acid lactone, while those of 4 exclude any γ or δ lactonic structure. In this case, the data are more in accordance with the 4-(2'-hydroxycyclohexyl)butanoic acid lactone structure.

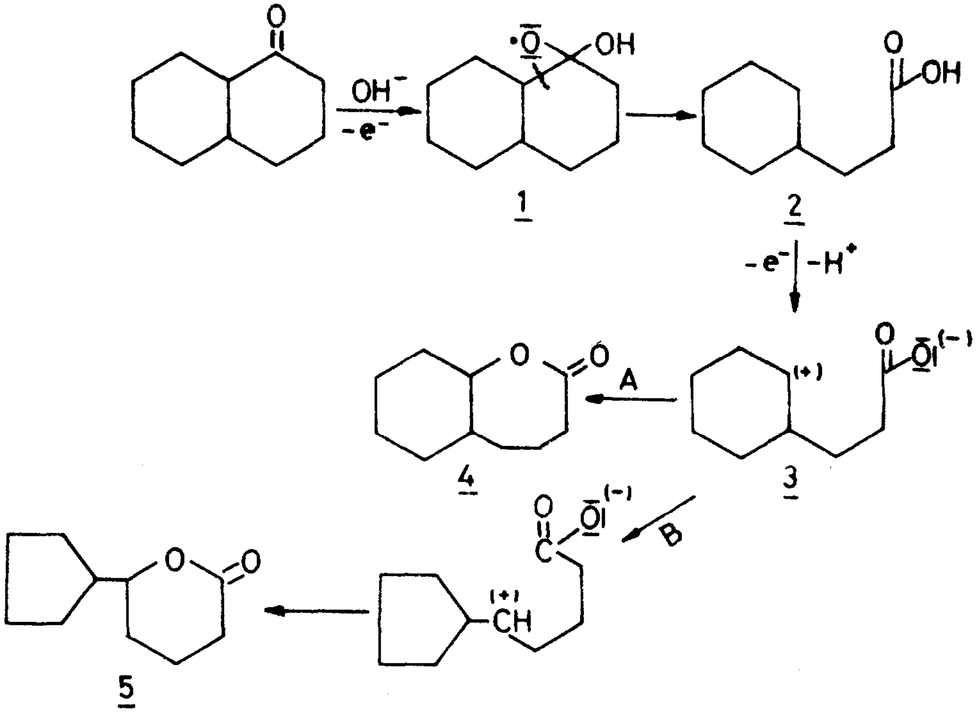
The 4 and 5 structures were confirmed by syntesis. The compound obtained by Baeyer-Villiger oxidation of the 2-cyclopentylcyclopentanone, (available from cyclopentanone[1]) with m-$ClPhCO_3H$ in Cl_3CH at 25°C, showed the same chromatographic and spectroscopic properties as the product 5 obtained by electrolysis. Baeyer-Villiger oxidation of 1-decalone gave a product with the same spectroscopic and chromatographic properties as product 4 obtained by electrolysis.

The electrolysis of 0,3 g of 1-decalone (6 Faradays/mol circulating with 0,3 A/cm^2 of current density) was carried out. At the end of each electrolysis, the solvent was removed on a rotary evaporator; water was added and the solution was acidified with concentrated hydrochloric acid, then extracted with ether.

The yields, determined by the standard internal chromatographic method, gave 47% of compound 5 and 14% of compound 4.

The formation of compounds 4 and 5 is rationalized in scheme 1. The step 1--2 is supported by the fact that ter-alkoxy free radicals cleave to give a carbonyl group and an alkyl free radical[2,3]. The intermediate 3 undergoes two processes: A) cyclisation to ε lactone 4 and B) ring contraction and cyclisation to give δ lactone 5.

Scheme 1



REFERENCES

1. "Beilsteins Handbuch der Organischen Chemie" Syst. n°617-618, Band VII, Springer-Verlag, Berlin (1931), (1968).

2. K. Maruyama and K. Marukami, Bull. Chem. Soc. Japan, 41, 1408(1968).

3. D.G. Heare and W.A. Waters, J. Chem. Soc., 2552(1964).

(Received in UK 16 November 1981)