

SHORT COMMUNICATIONS

KRATKA SAOPĆENJA

Note on the Preparation of 5-Phenyl-oxazolidine-2,4-dione

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5-Phenyl-oxazolidine-2,4-dione has been prepared by the condensation of ethyl mandelate with guanidine nitrate and subsequent hydrolysis of the 2-imino intermediate^{1, 2}; by condensing »acetone-mandelic acid«^{3, 4} or ethyl mandelate² with urethane; by the condensation of ethyl mandelate with urea⁵ or 1-acetyl-3-methyl-urea⁶; by the reaction of ethyl α -chloro-phenylacetate with urea or 1-acetyl-3-methyl-urea and subsequent hydrolysis⁷; by condensing mandelamide with diethyl carbonate⁸. 5-Phenyl-oxazolidine-2,4-dione was furthermore obtained by the alkaline hydrolysis of 1,5-diphenyl- and 1-methyl-5-phenyl-dialuric acid^{9,10} and 5-bromo-1,5-diphenyl- and 5-bromo-1-methyl-5-phenyl-barbituric acid with subsequent acid hydrolysis of the 2-imino-intermediates¹¹ and, by the action of alkali on 1-(phenyl-chloroacetyl)-3-phenyl-urea and (phenyl-chloroacetyl)-urea¹¹.

In accordance with Stoughton's interpretation of the course of the formation of oxazolidine-2,4-diones from α -hydroxy-esters and urea¹², we prepared the 5-phenyl-derivative by the cyclization of acetylmandelyl-urea with sodium ethoxide as condensing agent. The product thus obtained showed to be identical with samples of 5-phenyl-oxazolidine-2,4-dione prepared by the method of Aspelund⁵ and with samples prepared from ethyl mandelate and dicyandiamide with subsequent acid hydrolysis. Acetylmandelyl-urea was prepared by the method of Stoughton^{13,14}.

Acetylmandelyl-urea:

Acetylmandelyl-chloride¹⁵ (20,5 g., 0,096 mole) was added to a suspension of urea (14,4 g., 0,24 mole) in benzene (50 ml.) and the mixture refluxed for five hours. After removing the solvent under reduced pressure, the residue was treated with water, giving 11,8 g. of crude acetylmandelyl-urea, which after recrystallization from benzene/toluene melted at 155,5–156,3° (uncorr.).

Anal. 3,794 mg substance: 0,408 ml N₂ (29°C, 752 mm Hg)Calcd. for C₁₁H₁₂N₂O₄ (236,23) : N 11,87%,

Found : N 12,03%

5-Phenyl-oxazolidine-2,4-dione:

a) from acetylmandelyl-urea: Acetylmandelyl-urea (0,4 g., 0,0017 mole) was added to an ethanolic solution (15 ml) of sodium ethoxide (from 0,08 g., 0,0035 g-atom sodium) and the mixture refluxed for six hours. The solvent was removed under reduced pressure, the residue dissolved in water, and extracted with ether. Acidification of the ice-cooled aqueous layer with dilute hydrochloric acid yielded 5-phenyl-oxazolidine-2,4-dione (0,12 g.), which after recrystallization from hot water melted at 107–108°.

* The experimental part was carried out in collaboration with Nenada Kravica, Nevenka Sladović and Dorijan Jakulić.

b) from ethyl mandelate and dicyandiamide: A methanolic solution (37 ml) of sodium methoxide (from 1,84 g., 0,03 g-atom sodium) was gradually added to a boiling suspension of ethyl mandelate (9,0 g., 0,05 mole) and dicyandiamide (6,3 g., 0,075 mole) in methanol (18 ml) over a period of five hours with stirring. The suspension was refluxed for additional two hours and the solvent removed under reduced pressure. The residual crude cyanimino-intermediate was hydrolysed by boiling it for eight hours with diluted (1:2) sulfuric acid (50 ml). The cooled emulsion was extracted with ether and washed with water. After evaporation of the solvent solid 5-phenyl-oxazolidine-2,4-dione (6,9 g.) was obtained, which after triturating with petroleum-ether and recrystallization from water melted at 107—108°.

The microanalysis was carried out by Mrs. I. Guštak-Mašek at the Institute of Organic Chemistry, Technical Faculty, University of Zagreb.

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IZVOD

Bilješka o pripremi 5-fenil-oksazolidin-2,4-diona

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5-fenil-oksazolidin-2,4-dion priređen je ciklizacijom acetilmandelil-karbamida uz natrium etoksid kao kondenzaciono sredstvo, što se slaže sa Stoughtonovom predodžbom, da kod pripreme oksazolidin-2,4-diona kondenzacijom α -hidroksi-estera i karbamida primarno nastaje odgovarajući acil-ureid¹². Isti spoj priređen je i kondenzacijom etil mandelata i dicitandiamida uz natrium metoksid i naknadnom hidrolizom intermedijarnog cijanimino-derivata.

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