FORMATION OF PROLYLPROLINE HYDROBROMIDE UNDER THE CONDITIONS OF THE BROMINATION OF L-PROLINE

G. S. Mikaelyan and S. G. Agbalyan

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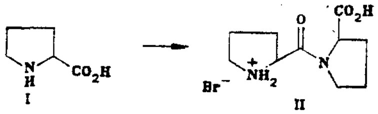
We studied the bromination of L-proline (I) with the object of synthesizing new pyrrolidine derivatives. It should be noted that when the aliphatic α-aminoacids are brominated in water, they are decarboxylated with the formation of the corresponding aldehydes [1].

It proved to be unexpected that the bromination of L-proline with bromine in CCl_4 or dioxane dibromide in $CHCl_3$ at 0-5°C leads to the formation of the optically inactive dipeptide hydrobromide — DL-prolylproline (II) — in up to 60% yield.



Hydrobromide (II). It has the mp 171-172°C (from methanol). The IR spectrum (in mineral oil) is as follows: 2700-2300, 1590 ($\overset{+}{N}H_2$), 1730 (C=O in COOH), and 1670 cm^{-1} (C=O amide). The PMR spectrum (D_2O) is as follows: 4.42 (broad t, J = 6.5 Hz, CO—CH—N), 3.51 (broad t, J = 6.5 Hz, CH_2—N), and 2.80-1.91 ppm (m, CH_2—CH_2); the integral intensities of the signals are 1:2:4 correspondingly. The data of the elemental analysis correspond with the calculated data.

It was noted that bromine also reacts with the salt (II) in the course of the reaction; this leads to the formation of a by-product in the form of an orange oil only containing the ionic bromine. The structure of the by-product is being defined more accurately.

The observed reaction can be regarded as a new single-step method for the synthesis of DL-prolylproline hydrobromide, not requiring the protection of the carboxyl and amino groups in the initial aminoacid.

LITERATURE CITED

1. L. Fieser and M. Fieser, Reagents for Organic Synthesis, Vol. 1, Wiley, New York (1979).

Institute of Organic Chemistry, Academy of Sciences of the Armenian SSR, Erevan 375,094. Translated from Khimiya Geterotsiklicheskikh Soedinenii, Vol 24, No. 3, p. 424, March, 1988. Original letter submitted April 1, 1987; revision submitted August 17, 1987.