3-Ethynylimidazo[1,2-*a*]BENZIMIDAZOLES

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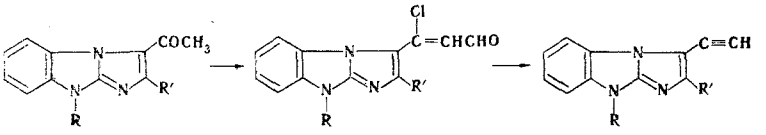
UDC 547.785.5:542.953

The previously unknown 3-ethynylimidazo[1,2-*a*]benzimidazoles (III) were obtained by reaction of 3-acetylimidazo[1,2-*a*]benzimidazoles (I) with phosphorus oxychloride in dimethylformamide (DMFA) and subsequent treatment of the reaction mixture with saturated potassium acetate solution.



I a-d II a III a-d

I-III a R=CH_3, R′=C_6H_5; b R=R′=CH_3; c R=$CH_2C_6H_5$, R′=CH_3; d R=$CH_2CH_2N(C_2H_5)_2$, R′=C_6H_5

The reaction proceeds through a step involving the formation of chlorovinyl aldehydes II, which are readily saponified to III under the reaction conditions. We were able to isolate intermediate II only in the case of 9-methyl-2-phenylimidazo[1,2-*a*]benzimidazole by carrying out the reaction at 10°C and by treatment of the reaction mixture with 10% potassium acetate solution. The structure of the compounds obtained was confirmed by the results of elementary analysis, the IR spectra, and also by synthesis of derivatives involving the acetylenic group. Bands of stretching vibrations of the C≡C bond appear at 2210 cm^{-1}, and bands of the ≡C−H bond appear at 3305-3310 cm^{-1} in the IR spectra of III.

EXPERIMENTAL

9-Alkyl(aralkyl)-2-aryl(alkyl)-3-ethynylimidazo[1,2-*a*]benzimidazoles (III). A solution of 1.5 ml (16 mmole) of phosphorus oxychloride in 5 ml of DMFA was added slowly with stirring in a stream of nitrogen to a solution of 5 mmole of 3-acetyl derivative I in 25 ml of (DMFA); the phosphorus oxychloride solution was added in such a way that the temperature of the reaction mixture did not rise above 25-30°. After all of the phosphorus oxychloride had been added, the mixture was stirred at room temperature for 0.5 h and then at 60-70° for 2 h. After this, the hot solution was treated with 25 ml of saturated potassium acetate solution while continuing stirring in a stream of nitrogen for another 1-1.5 h. The resulting precipitate was removed by filtration and washed with water to give the product in 70-85% yield. The compounds were obtained as yellow-toned crystals with mp 127-128° for III (dec., petroleum ether), 117-118° (dec., petroleum ether) for IIIb, and 170° (alcohol) for IIIc. Compound IIId was isolated in the form of the dipicrate with mp 168-169°, inasmuch as the base and the acetate are oils.

Chlorovinyl Aldehyde IIa. This compound was obtained as bright-yellow needles with mp 155-156° (petroleum ether). IR spectrum: $\nu_{C=O}$ 1625, ν_{C-Cl} 920 cm^{-1} (see [1]).

LITERATURE CITED

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Rostov State University. Scientific-Research Institute of Physical and Organic Chemistry, Rostov-on-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1577-1578, November, 1974. Original article submitted April 30, 1974.