cm, l 25 cm) L40/100 with elution by a 1:19 acetone—chloroform mixture, 0.08 g (52%) of compound Ia was isolated. Oil, R_f 0.78 (B).

dl-2-(trans-3-Hydroxyocten-1-yl)-N-(6-ethoxycarbonylhexyl)indole (Ib) was obtained and isolated in the same way as Ia. A 0.1 g (20 mmole) portion of $NaBH_4$ and 20 ml of 70% 2-propanol were added to 0.32 g (0.8 mmole) of ketone IVb. After chromatographic purification, 0.18 g (56%) of compound Ib was obtained. Oil, R_f 0.73 (B).

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NEW SYNTHESIS OF INDOLE-7-CARBOXYLIC ACID

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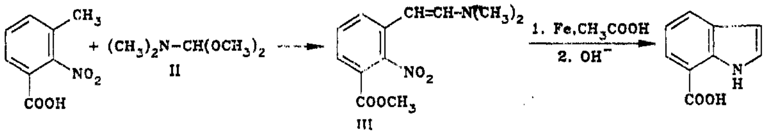
UDC 547.757.07

A new preparative method for the synthesis of indole-7-carboxylic acid has been developed, consisting in reductive cyclization of β-(dimethylamino)-3-carbomethoxy-2-nitrostyrene by the action of iron in acetic acid.

Indole-7-carboxylic acid is used in the synthesis of optical filter dyes, used for the protection of an exposed light-sensitive material fogging during its treatment in light [1, 2]. The known methods for the preparation of this compound are multistep and proceed with a low overall yield, which does not exceed 20% [3, 4].

In developing a new variant of the synthesis of indole-7-carboxylic acid [5], free of the above drawbacks, we used the method of constructing the indole ring, consisting in a reductive cyclization of β-(dialkylamino)-2-nitrostyrenes [6]. The latter compounds are most conveniently obtained by the condensation of substituted o-nitrotoluenes with DMFA dialkyl acetals [7]. In accordance with this, we selected 2-nitro-m-toluic acid (I) as the starting compound.



When acid I is heated with dimethyl acetal (II) in DMFA, an esterification of the carboxyl group takes place together with the formation of an enamine grouping. Reduction of enamine III by iron in acetic acid gives methyl indole-7-carboxylate, which, without purification, is hydrolyzed by boiling with an aqueous solution of sodium hydroxide. The overall yield of indole-7-carboxylic acid is thus 60%.

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EXPERIMENTAL

The IR spectra were run in mineral oil on a UR-20 spectrophotometer.

β-(Dimethylamino)-3-carbomethoxy-2-nitrostyrene. A mixture of 9 g (0.05 mole) of 2-nitro-m-toluic acid [8], 32.5 ml (0.25 mole) of DMFA dimethyl acetal [9] and 50 ml of DMFA is heated in an argon atmosphere to 130-140°C for 24 h. The red solution formed is evaporated under vacuum, using an aspirator, and water is added to the residue. The precipitate is filtered, washed with water, and dried. Yield, 9.3 g (74%), mp 131°C (from isopropanol). IR spectrum: 1720 (C=O), 1635 (C=C), 1530, 1290 cm^{-1} (NO_2). Found: C 57.4; H 5.8; N 11.2%. $C_{12}H_{14}N_2O_4$. Calculated: C 57.6; H 5.6; N 11.2%.

Indole-7-carboxylic acid. A mixture of 75 g of β-(diethylamino)-3-carbomethoxy-2-nitrostyrene, 180 g of iron powder, 800 ml of ethanol, and 80 ml of acetic acid is heated, with vigorous stirring, on a water bath. When the temperature in the flask reaches 50°C, the bath is removed, and the mixture spontaneously heats up to 80°C. This temperature is maintained by a cold water bath until the end of the exothermal reaction, after which the flask contents are heated for another 30 min. The reaction mixture is cooled, 4.5 liters of water are added, and the unreacted iron is filtered off. The residue on the filter is washed thoroughly with benzene, and the aqueous filtrate is extracted 3 times with benzene. The combined organic extracts are washed with water and saturated sodium carbonate solution, and dried over sodium sulfate. Benzene is distilled off, and a solution of 35 g of sodium hydroxide in 310 ml of water is added to the residue. The mixture is boiled for 5.5 h, then cooled, filtered, and acidified with hydrochloric acid to pH 2. The precipitate of indole-7-carboxylic acid is filtered, washed with water, and dried. Yield 38.5 g (80%), mp 205-206°C (from an ethanol—water mixture). IR spectrum: 3420 (N—H), 1670 cm^{-1} (C=O).

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