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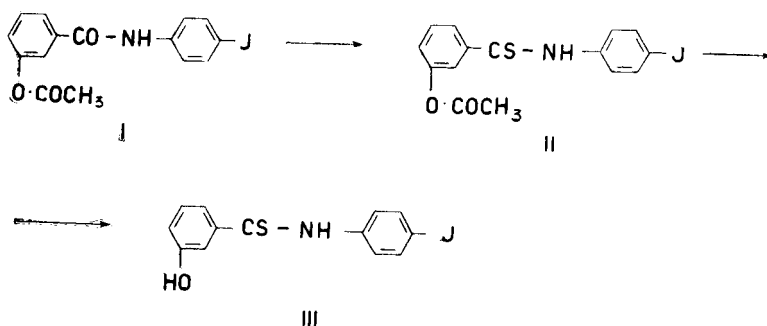
A CONTRIBUTION TO THE KNOWLEDGE OF THIOAMIDES

Synthesis of the 3-Hydroxy-4'-iodothiobenzanilide

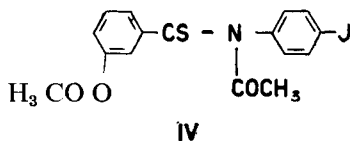
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No positive results were obtained, when introducing the iodine into 3-Hydroxythiobenzanilide through its Acetoxy-thioderivative¹). In all cases there sulphurless compounds were obtained. For this reason a synthesis of 3-Hydroxy-4'-iodothiobenzanilide was performed in another way.

At first, according to the Schotten-Baumann method 3-Acetoxy-4'-iodobenzanilide (I) (colourless needles, m.p. 182—183°C) was obtained. In the second phase of the reaction treatment of the compound (I) with phosphorus pentasulfide in dry organic solvent-xylene^{3,4}) corresponding 3-Acetoxy-4'-iodothiobenzanilide (II) (yellow leaves m. p. 125—126°C) was acquired. At the end, under mild conditions of hydrolysis using dilute aqueous sodium hydroxyde 3-Hydroxy-4'-iodothiobenzanilide (III) (light yellow prisms, m.p. 215—216°C) was obtained. The scheme of the synthesis is as follows:



The presence of the free hydroxy group in the compound (III) was proved by acetylation with acetic anhydride. By this treatment the thioamide group was acetylated as well, and the corresponding O, N-Diacetyl-3-hydroxy-4'-iodothiobenzanilide (IV) (orange needles, m. p. 90—91°C) was obtained, which according to the earlier research of Hydroxythioamides^{4,5} has the following structure:



The same compound (IV) can be obtained with acetylation of the compound (III) as well.

EXPERIMENTAL

The melting points are uncorrected.

3-Acetoxy-4'-iodobenzanilide (I)

3,96 g (0,02 mole) 3-Acetoxybenzoyl chloride⁶) (fresh prepared) was added in drops and by constant mixing in cool solution on 0°C from the 4,38 g (0,02 mole) p-iodoaniline⁷) in 12 ml pyridine for 15 minutes. After standing for an hour at room temperature from the reaction mixture a colourless crystal product was separated, filtered, washed and dried in air. By that 7,9 g (98,4%) of crude product with m. p. 173—174°C was obtained. This recrystallization from ethanol gives 3-Acetoxy-4'-iodobenzanilide colourless needles with m.p. 182—183°C.

Analysis: 4,064 mg subst. 6,998 mg CO₂, 1,162 mg H₂O
4,692 mg subst. 0,147 ml N₂ (750 mm 24°C)

C₁₅H₁₂NO₃J (381,18)

Calc.: C 47,28, H 3,17, N 3,68%
Found.: C 46,99, H 3,19, N 3,55%

3-Acetoxy-4'-iodothiobenzanilide (II)

In heated solution from 1,9 g (0,005 mole) 3-Acetoxy-4'-iodobenzanilide (I) in 15 ml dry xylene 1,2 g (0,005 mole) finely powdered phosphorus pentasulfide was added. The reaction mixture was refluxed over the oil bath at the temperature of 120—130°C for 15—20 minutes. The colour of the solution was changing from yellow to red and laterly to dark red. The change of the colour showed that the reaction was going correctly. The warm reaction mixture was immediately filtered and by cooling it a yellow crystal product was obtained. This product was filtered, washed and dried. 2,9 g (92,43%) of crude product with m.p. 121—122°C was obtained. By recrystallization from ethanol yellow leaves with mp. 125—126°C, were formed.

Analysis: 3,882 mg subst. 6,432 mg CO₂, 1,002 mg H₂O
4,551 mg subst. 0,127 ml N₂ (750 mm 24 °C)

C₁₅H₁₂NO₂SJ (397,25)

Calc.: C 45,38, H 3,05, N 3,53%
Found.: C 45,21, H 2,89, N 3,17%

3-Hydroxy-4'-iodothiobenzanilide (III)

A mixture of 1,98 g (0,005 mole) 3-Acetoxy-4'-iodothiobenzanilide (II) and 20 ml of diluted alkali (In NaOH) was heated on the water bath for 10—15 minutes at the temperature of 60—70°C. The yellow alkali solution (pH 8—9) was filtered, cooled and acidised with dilute hydrochloric acid (In HCl) to pH 6—7. By that, yellow precipitate was obtained which by cooling, immediately got crystallised. The crude product was filtered, washed with water and dried. 0,8 g (89,46% of crude product with m.p. 210—211°C was obtained. By recrystallization from ethanol yellow prisms were separated with m.p. 215—216°C.

Analysis: 6,903 mg subst. 11,174 mg CO₂, 1,704 mg H₂O
5,006 mg subst. 0,167 ml N₂ (750 mm 24°C)

C₁₃H₁₀NO₂SJ (355,204)

Calc.: C 43,98, H 2,84, N 3,95%
Found.: C 44,15, H 2,76, N 3,83%

O, N-Diacetyl-3-hydroxy-4'-iodothiobenzanilide (IV)

In the mixture of 1,77 g (0,005 mole) 3-Hydroxy-4'-iodothiobenzanilide (III) and 6 ml dry pyridin dropwise, while constantly stirring 6 g (0,06 mole) acetic anhydride was added. After standing overnight at room temperature, the dark red reaction mixture was poured into 300 ml iced water. In that way an orange crystal product was separated, which was then filtered, washed with water and dried. 0,95 g (85,92%) of crude product was obtained with m.p. 87—88°C. By recrystallization from ethanol-water (2:1) it gives orange needles with m.p. 90—91°C.

Analysis: 4,891 mg subst. 8,398 mg CO₂, 1,377 mg H₂O
4,931 mg subst. 0,137 ml N₂ (750 mm 24°C)

C₁₇H₁₄NO₃SJ (439,28)

Calc.: C 46,51, H 3,23, N 3,19%
Found.: C 46,86, H 3,15, N 3,15

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Скопје

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ПРИЛОГ КОН ПОЗНАВАЊЕТО НА ТИОАМИДИТЕ

Сингеза на 3-хидрокси-4'-јодтиобензанилид

ИЗВОД

При обид да се внесе јод во 3-хидрокси-тиобензанилидот не се добиени позитивни резултати. Секој пат се добиваат соединенија без сулфур- Затоа синтезата на 3-хидрокси-4'-јодтиобензанилидот е извршена на друг начин.

Од 3-ацетокси-4'-јодбензанилид (I) (безбојни иглици, т.т. 182—183°C) со помош на фосфорен пентасулфид во сув ксилол е добиен 3-ацетокси-4'-јодтиобензанилид (II) (жолти ливчина, г.т. 125—126°C). Од него со умерена алкална хидролиза е добиен 3-хидрокси-4'-јодтиобензанилид (III) (жолти призми, г.т. 215—216°C). Присуството на слободната хидроксилна група во соединението (III) е докажано со ацетитирање со анхидрид на оцетна киселина. На тој начин е добиен О, N-диацетил-3-хидрокси-4'-јодтиобензанилид (IV) (оранжови иглици, т.т. 90—91°C).