SYNTHESIS OF 2-METHYL-5-PHENYLTHIENO[2,3-d]THIAZOLE

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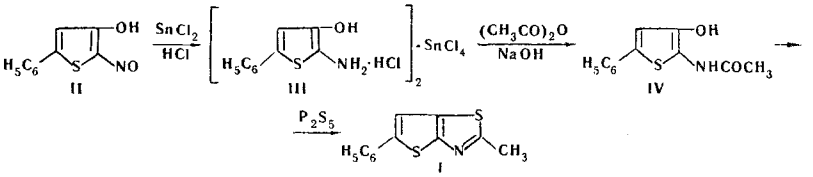
UDC 547.789.6

The synthesis of a new heterocyclic base – 2-methyl-5-phenylthieno[2,3-d]thiazole – is described.

Polymethine dyes, which are derivatives of the isomeric 2-methylthienothiazoles [1,2] are of definite interest as optical sensitizers of photographic silver halide emulsions [3,4].

In this connection, it seemed of interest to synthesize a new heterocyclic base with a condensed thiophene ring – 2-methyl-5-phenylthieno[2,3-d]thiazole (I) – in order to obtain polymethine dyes of various classes from it and to study their coloration and sensitizing action.

This base was obtained from 2-nitroso-3-hydroxy-5-phenylthiophene (II) via the scheme



Reduction of II with stannous chloride in concentrated hydrochloric acid gave the double stannic chloride salt of 2-amino-3-hydroxy-5-phenylthiophene hydrochloride (III), which was converted to 2-acetamido-3-hydroxy-5-phenylthiophene (IV) by reaction with acetic anhydride in alkali. Heating IV with phosphorus pentasulfide gave I, which readily forms quaternary salts on reaction with alkylating agents.

EXPERIMENTAL

2-Nitroso-3-hydroxy-5-phenylthiophene (II). This was obtained in 90% yield by nitrosation of 3-hydroxy-5-phenylthiophene via the method in [5]. It was isolated as yellow plates (from ethanol) with mp 215-216 deg (216 deg [5]).

Double Stannic Chloride Salt of 2-Amino-3-hydroxy-5-phenylthiophene Hydrochloride (III). Pulverized II [40 g (0.2 mole)] was added in small portions with vigorous stirring to a solution of 200 g of stannous chloride in 250 ml of concentrated hydrochloric acid at 35-40 deg. At the end of the addition the reaction mixture was stirred at the same temperature for 3 h and cooled. The resulting precipitate was filtered, washed with alcohol, and ether, and air-dried to give 40% of yellowish crystals (from ethanol).

2-Acetamido-3-hydroxy-5-phenylthiophene (IV). A solution of 21 ml of acetic anhydride in 30 ml of ether was added with vigorous stirring to a suspension of 30 g (0.04 mole) of III in 210 ml of water at 0 to 5 deg. A solution of 40 g of sodium hydroxide in 60 ml of water was then added in small portions to the mixture at the same temperature. At the end of the addition the mixture was stirred for 30 min with ice-water cooling, and the ether was removed with an air stream. The residue was filtered and the filtrate was acidified with dilute (1:1) hydrochloric acid. The resulting precipitate was filtered, washed with water, and dried to give 14.8 g (75%) of light-brown prisms (from 50% alcohol in the presence of activated charcoal) with mp 146-147 deg. Found %: N 5.79, 5.87. $C_{12}H_{11}NO_2S$. Calc. %: N 6.00.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, 1624-1625, December, 1970. Original article submitted September 29, 1969.

2-Methyl-5-phenylthieno[2,3-d]thiazole (I). A thoroughly ground mixture of 15 g (0.064 mole) of IV and 15 g of phosphorus pentasulfide was heated at 130-140 deg for 8-10 min. The brown melt obtained was treated with 300 ml of water, and the mixture was cooled and made alkaline with 25% sodium hydroxide until it gave an alkaline reaction to litmus. The base was steam distilled from the reaction mixture. The distillate was treated with ether, the ether extract was dried over calcined potassium carbonate, and the ether was removed to give 3.64 g (26%) of colorless plates (from petroleum ether) of I with mp 118-119 deg. Found %: N 6.13, 6.26. $C_{12}H_9NS_2$. Calc. %: N 6.05. The ethiodide was obtained as colorless prisms (from absolute ethanol) with mp 130-131 deg. Found %: N 3.63, 3.71. $C_{14}H_{14}INS_2$. Calc. %: N 3.62.

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