SYNTHESIS OF 7,8,8-TRIMETHYLTHIENO-[3,2-e]INDOLENINE

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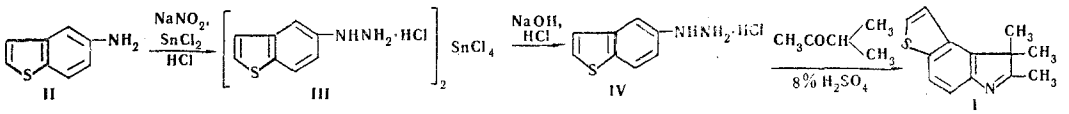
The synthesis of a new heterocyclic base 7,8,8-trimethylthieno[3,2-e]indolenine is described.

We previously [1] described the synthesis of 4,4,5-trimethylthieno[2,3-b]- and -[3,2-b]pyrrolenines. In this communication we describe the synthesis of 7,8,8-trimethylthieno[3,2-e]indolenine (I), which is the starting compound for the synthesis of various classes of polymethine dyes. Base I was synthesized from 5-aminothionaphthene (II) via the scheme



II III IV I

The double tin salt (III) of 5-thionaphthenylhydrazine hydrochloride was obtained by diazotization of II with sodium nitrite in hydrochloric acid with subsequent reduction of the diazonium compound thus formed with stannous chloride. 5-Thionaphthenylhydrazine hydrochloride (IV) was synthesized by treatment of III with sodium hydroxide solution and subsequent addition of an ether solution of hydrogen chloride to an anhydrous ether solution of the base of IV. Compound I was synthesized in 11.6% yield by the condensation of IV with methyl isopropyl ketone in dilute sulfuric acid.

Base I is a light-yellow oil with bp 174-177 deg (6 mm) and forms a picrate and quarternary salts.

EXPERIMENTAL

Double Tin Salt of 5-Thionaphthenylhydrazine Hydrochloride (III). A solution of 4.8 g of sodium nitrite in 30 ml of water was added with stirring to a suspension of 15 g of the sulfate of II in 570 ml of concentrated hydrochloric acid at 0-5 deg. The mixture was stirred for 1.5-2 h, and 60 g of pulverized stannous chloride was added with vigorous stirring to the thus obtained solution of diazonium salt at 0-5 deg. The mixture was stirred for 3 h and allowed to stand at room temperature overnight. The resulting precipitate was filtered; washed with concentrated hydrochloric acid, alcohol, and ether; and air-dried to give 12.2 g (48%) of colorless prisms from ethanol with mp > 300 deg.

5-Thionaphthenylhydrazine Hydrochloride (IV). A 20% solution of sodium hydroxide was added to a suspension of 16 g of III in 200 ml of water with stirring and ice-water cooling until the mixture was alkaline to litmus. The mixture was allowed to stand with cooling for 1.5-2 h, and the resulting precipitate was filtered, washed thoroughly with ice water, and dried. The product was dissolved in ether; and the ether solution was filtered, dried over potassium carbonate; and the ether was removed by vacuum distillation. The residue was treated with dry petroleum ether. The insoluble residue was filtered, dissolved in dry ether; and an ether solution of anhydrous hydrogen chloride was added gradually to the ether solution until precipitation was complete. The precipitate was filtered, washed thoroughly with dry ether, and dried in vacuo to give 3.9 g (81%) of colorless prisms (from ethanol) with mp 211-212 deg. Found %: N 13.90, 14.16. $C_8H_9ClN_2S$. Calc. %: N 13.95.

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7,8,8-Trimethylthieno[3,2-e]indolenine (I). Methyl isopropyl ketone (10 g) was added dropwise with vigorous stirring to a solution of 19 g of IV in 300 ml of 8% sulfuric acid at 92-95 deg. The mixture was stirred at 92-97 deg for 2.5 h, cooled, made alkaline with dilute sodium hydroxide, and the base was steam-distilled. The distillate was shaken with ether, and the ether solution was dried over potassium carbonate, the ether was removed by distillation, and the residue was vacuum-distilled to give 2.5 g (11.6%) of a light-yellow oil with bp 174-177 deg (6 mm). Found %: N 6.34, 6.39; C 72.49, 72.56. $C_{13}H_{13}NS$. Calc. %: N 6.48; C 72.52. The ethiodide was obtained as colorless plates (from anhydrous ethanol) with mp 249-250 deg. Found %: N 3.94, 4.10. $C_{15}H_{18}INS$. Calc. %: N 3.77. The picrate was obtained as light-yellow needles (from ethanol) with mp 179-180 deg. Found %: N 6.49, 6.56. $C_{19}H_{16}N_4O_7S$. Calc. %: N 6.50.

LITERATURE CITED

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2. L. F. Fieser and R. G. Kennely, J. Am. Chem. Soc., 57, 1611 (1935).