SYNTHESIS OF 2-METHYLTHIONAPHTHENO[2,3-d]-IMIDAZOLE

P. I. Abramenko

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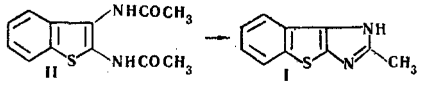
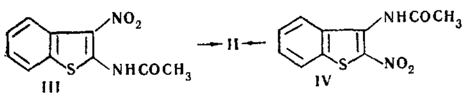
The synthesis of a new heterocyclic base 2-methylthionaphtheno[2,3-d]imidazole is described.

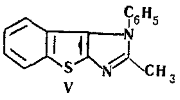
2-Methylthionaphtheno[2,3-d]imidazole (I) can serve as the starting material for the preparation of polymethine dyes of various classes. This compound was synthesized by us in 69% yield by cyclization of 2,3-diacetamidothionaphthene (II) on heating:



Base I readily forms a picrate and a quaternary salt.

Compound II is obtained by reduction of 3-nitro-2-acetamido- (III) or 2-nitro-3-acetamidothionaphthene (IV) [1] with zinc dust in a mixture of acetic acid and acetic anhydride.





Compounds III and IV are obtained by nitration of 2- or 3-acetamidothionaphthene [2, 3], respectively, by heating with dilute nitric acid.

We proposed the synthesis of the N-substituted base 1-phenyl-2-methylthionaphtheno[2,3-d]imidazole (V) from 2-nitro-3-bromothionaphthene (VI) [4]. 2-Nitro-3-phenylaminothionaphthene (VII) is obtained by the action of aniline on VI during heating and is reduced with zinc dust in an acetic-acid medium to 2-acetamido-3-phenylaminothionaphthene (VIII). However, we were unable to select the successful temperature conditions, solvent, and condensing agent for the cyclization of VIII to V.

EXPERIMENTAL

2-Nitro-3-acetamidothionaphthene (IV). This was obtained in 86% yield by reaction of dilute nitric acid with 3-acetamidothionaphthene and had mp 206-207° (from ethanol). According to [1], IV has mp 205°.

2-Acetamido-3-nitrothionaphthene (III). Concentrated nitric acid (40 ml) was added to a suspension of 10 g of 2-acetamidothionaphthene in 300 ml of water. The mixture was heated on a boiling water bath for 30 min, cooled, and the resulting precipitate was filtered to give 11.5 g (73%) of light-yellow needles (from ethanol) with mp 219-220°. Found %: N 11.79, 11.93. $C_{10}H_8N_2O_3S$. Calculated %: N 11.85.

2,3-Diacetamidothionaphthene (II). A. Zinc dust (100 g) was added with vigorous stirring to a mixture of 18 g of IV, 360 ml of acetic acid, and 240 ml of acetic anhydride. The mixture was then stirred for 3-4 h at 70-80°, diluted with 200 ml of acetic acid, and filtered. The filtrate was evaporated in vacuo to dryness. The residue was treated with water, and the precipitate was filtered to give 17.5 g (92%) of colorless plates (from 80% alcohol) with mp 274-275°. Found %: N 11.20, 11.21. $C_{12}H_{12}N_2O_2S$. Calculated %: N 11.20.

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B. Zinc dust (80 g) was added in small portions with vigorous stirring to a solution of 15 g of III in a mixture of 300 ml of glacial acetic acid and 180 ml of acetic anhydride at 40-45°. The mixture was stirred at the same temperature for 1 h, at 50-55° for 2 h, diluted with 180 ml of acetic acid, and treated in the manner described above to give 12.6 g (80%) of II.

2-Methylthionaphtheno[2,3-d]imidazole (I). Compound II (12.4 g) was heated at 290-310° for 25-30 min (until distillation of a mixture of water and acetic acid ceased). The fused mass was cooled to 90-100° and dissolved by heating in dilute (1 : 1) hydrochloric acid. The precipitate of the base hydrochloride that precipitated on cooling was filtered and washed with water to give 8.5 g (76%) of colorless crystals (from water) with mp 324-326°. Found %: N 12.31, 12.45. $C_{10}H_9ClN_2S$. Calculated %: N 12.46.

The hydrochloride (11.2 g) was dissolved in water, the solution was neutralized with sodium bicarbonate, and the precipitate was filtered to give 8.6 (91%) of colorless plates (from 50% alcohol) with mp 234-235°. Found %: N 14.78, 14.96. $C_{10}H_8N_2S$. Calculated %: N 14.88. The picrate was obtained in the form of light-yellow prisms (from ethanol) with mp 255-256°.

3-Phenylamino-2-nitrothionaphthene (VII). A mixture of 5.2 g of VI [4] and 6 ml of aniline was heated on a boiling water bath for 6 h, cooled, and the resulting precipitate was filtered to give 5.2 g (96%) of orange prisms (from ethanol) with mp 205-206°. Found %: N 10.38, 10.49. $C_{14}H_{10}N_2O_2S$. Calculated %: N 10.36.

3-Phenylamino-2-acetamidothionaphthene (VIII). Zinc dust (10 g) was added in small portions with stirring in the course of 30 min to a mixture of 5.4 g of VII, 50 ml of acetic acid, and 20 ml of acetic anhydride at 50-60°. The reaction mass was stirred at 70-80° for 4 h, diluted with 20 ml of acetic acid, and filtered. The filtrate was evaporated to dryness in vacuo, the residue was treated with water, and the precipitate was filtered to give 5.1 g (91%) of colorless plates (from 80% alcohol) with mp 212-213°. Found %: N 10.26, 10.23. $C_{16}H_{14}N_2OS$. Calculated %: N 9.92.

LITERATURE CITED

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4. E. B. Middleton and G. A. Dawson, US Patent No. 2,424,483 (1947); Chem. Abstr., 41, 6483 (1947).