BRIEF COMMUNICATIONS

SYNTHESIS OF 2-METHYLPHENANTHRO[2, 1-d]THIAZOLE

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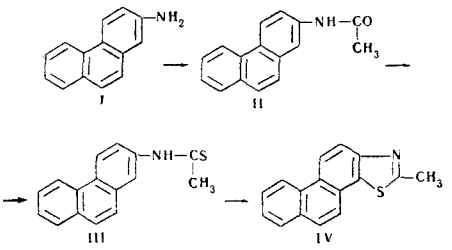
2-Methylphenanthro[2, 1-d]thiazole has been synthesized by the oxidative cyclization of 2-thioacetylaminophenanthrene.

In continuation of our previous investigations [1], we have synthesized the first homolog of phenanthro[2, 1-d]thiazole, containing a methyl group in position 2. For the synthesis we used the method [2] employed previously in this series to obtain 2-methylphenanthro [9, 10-d]thiazole [3]. Starting from 2-aminophenanthrene (I) [4], by its acetylation with acetic anhydride in pyridine solution we obtained 2-acetylaminophenanthrene (II) in almost quantitative yield and this was then converted into 2-thioacetylaminophenanthrene (III) by reaction with phosporus pentasulfide:



2-Methylphenanthro[2, 1-d]thiazole (IV) was synthesized from III by cyclization in ethanolic alkaline solution in the presence of potassium ferricyanide.

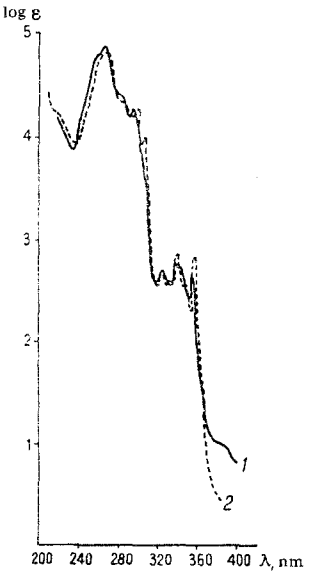
The figure shows the UV spectra of compound IV and of phenanthro[2, 1-d]thiazole [1].

EXPERIMENTAL

2-Acetylaminophenanthrene (II) was obtained from 2-aminophenanthrene [4] by acetylation with acetic anhydride in pyridine at room temperature. Yield 98%. Colorless crystals, mp 224°-226° C.

2-Thioacetylaminophenanthrene (III). With stirring, 1.0 g (0.0045 mole) of powdered phosphorus pentoxide was slowly added to a boiling solution of 1.0 g (0.0042 mole) of 2-acetylaminophenanthrene in 250 ml of anhydrous p-xylene. The reaction mixture was boiled for 1 hr. The hot xylene solution was decanted off and concentrated to small bulk. On cooling, 0.6 g (56%) of substance III deposited. After recrystallization from ethanol (with carbon), lustrous colorless plates were obtained with mp 178°-179° C. Found, % C 76.17; H 4.93; S 12.34%. Calculated for $C_{16}H_{13}NS$, %: C 76.49; H 5.18; S 12.75%.

2-Methylphenanthro[2, 1-d]thiazole (IV). A suspension of 0.37 g of III in 7.5 ml of methanol heated to boiling was treated with 15 ml of 10% NaOH. The thioacetylamino compound went into solution and, after the solution had been filtered, it was treated slowly with stirring with a solution of 3.7 g of potassium ferricyanide in 15 ml of water. On the following day the precipitate was filtered off and recrystallized from methanol. Yield 0.21 g (62%). Colorless plates, mp 172°-173° C (from acetone). Found, %: C 77.05; H 4.63%. Calculated for $C_{16}H_{11}NS$, %: C 77.11; H 4.42%. Picrate—yellow silky needles, mp 209.5°-210° C (from ethanol). Found, %: C 55.63; H 3.20; N 11.99%. Calculated for $C_{16}H_{11}NS \cdot C_6H_3N_3O_7$, %: C 55.23; H 2.92; N 11.72%.



UV spectra of: 1) 2-methylphenanthro[2, 1-d]thiazole (IV); 2) phenanthro[2, 1-d] thiazole.

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