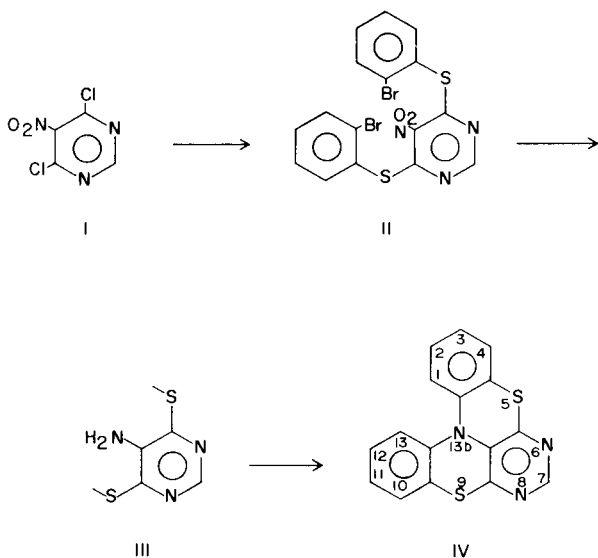


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## Synthesis of 5,9-Dithia-6,8,13b-triazanaphth[3,2,1-de]anthracene (I)

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In the search for compounds with potential hypotensive activity, an attempt was made to synthesize 2,4-diazaphenothiazines (3a-c). The first step in one of our projected syntheses involved the reaction of 4,6-dichloro-5-nitropyrimidine (I) with 2-bromothiophenol. Instead of the desired 4-(2'-bromophenylthio)-6-chloro-5-nitropyrimidine the only pure product isolated from the reaction, even with a large excess of the pyrimidine, was 4,6-di-(2'-bromophenylthio)-5-nitropyrimidine (II). Reduction of the nitro group of II to the amine III, followed by cyclization, gave 5,9-dithia-6,8-13b-triazanaphth[3,2,1-de]anthracene (IV).



## EXPERIMENTAL

## 4,6-Di-(2'-bromophenylthio)-5-nitropyrimidine.

To 2-bromothiophenol (4) (11.34 g., 0.06 mole) in 18 ml. of absolute ethanol was added 3 ml. of aqueous sodium hydroxide (40 g./50 ml.). The solvent was removed under vacuum and the residual

sodium salt, dissolved in 45 ml. of absolute ethanol, was added dropwise to a stirred solution of 4,6-dichloro-5-nitropyrimidine (5) (5.8 g., 0.06 mole) in 25 ml. of absolute ethanol at room temperature. The mixture was refluxed for two hours during which a yellow precipitate appeared. The precipitate was collected, washed with water and air dried. Crystallization from benzene-acetone yielded 12.4 g., 84%, of 4,6-di-(2'-bromophenylthio)-5-nitropyrimidine as yellow crystals melting at 193-196°. An analytical sample crystallized several times from acetone melted at 200-201°.

*Anal.* Calcd. for  $C_{16}H_{11}Br_2N_3O_2S_2$ : C, 38.49; H, 1.82; N, 8.42. Found: C, 38.36; H, 2.08; N, 8.66.

## Reduction of 4,6-di-(2'-bromophenylthio)-5-nitropyrimidine.

Ten and thirty-six hundredths grams (0.021 mole) of 4,6-di-(2'-bromophenylthio)-5-nitropyrimidine was added in small portions to a stirred solution of  $SnCl_2 \cdot 2H_2O$  (29 g., 0.13 mole) in 26 ml. of concentrated HCl at a rate to maintain the internal temperature at 50 to 60°. The solution was then stirred and refluxed for three hours during which time some insoluble oil appeared. The mixture was diluted with water and the organic phase was separated. The oil which solidified on cooling was crystallized from ethanol giving 4.7 g. (50%) of product melting at 138-143°. Further crystallization from ethanol raised the melting point to 155-156°.

*Anal.* Calcd. for  $C_{16}H_{11}Br_2N_3S_2$ : C, 40.95; H, 2.36; N, 8.96. Found: C, 41.27; H, 2.57; N, 9.13.

## 5,9-Dithia-6,8,13b-triazanaphth[3,2,1-de]anthracene.

A mixture of 4,6-di-(2'-bromophenylthio)-5-aminopyrimidine (8.2 g., 0.0175 mole) and 0.4 g. of copper powder in 85 ml. of refluxing dimethylformamide was stirred under nitrogen for 20 hours. The mixture was cooled and filtered. The filtrate was poured into water and the greenish-yellow suspension was filtered and the filtrate extracted with ether. The residues from the filtration and from evaporation of the ether extract were combined and crystallized from *iso*-propyl ether. The yield of product melting at 175-178° was 2.55 g., 48%. An analytical sample crystallized from ethanol melted at 186-187°.

*Anal.* Calcd. for  $C_{18}H_9N_3S_2$ : C, 62.57; H, 2.95; N, 13.61. Found: C, 62.35; H, 3.08; N, 13.75.

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