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Synthesis of 2-Aminonaphthalene-1-thiol and Its Conversion into 8-Nitro-7*H*-benzo[*c*]phenothiazine

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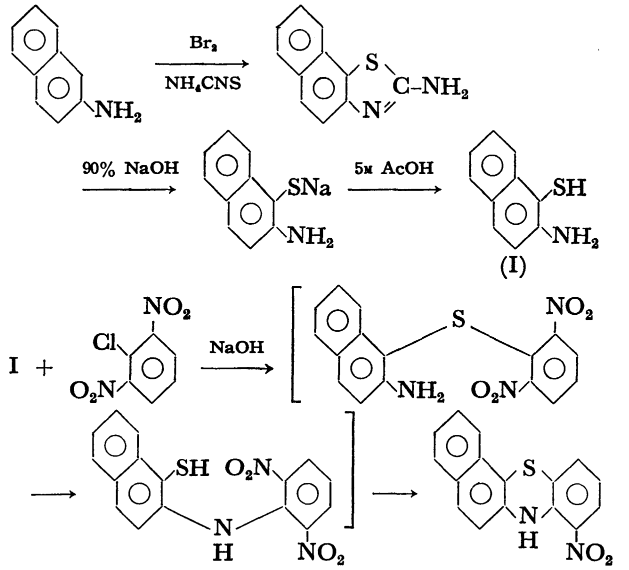
Synopsis. Synthesis of 2-Aminonaphthalene-1-thiol by hydrolytic cleavage of 2-aminonaphtho(2′,1′: 4, 5)thiazole and its conversion into 8-nitro-7*H*-benzo[*c*]phenothiazine *via* Smiles rearrangement *in situ* are reported.

Phenothiazines form an interesting series for Pharmaceutical and industrial uses[1,2] and physical studies.[3] A large number of phenothiazines have been synthesized, but there is no report on the synthesis of 7*H*-benzo[*c*]phenothiazine and its substituted products. Phenothiazines are generally synthesized by condensation of *o*-aminobenzenethiols with *o*-halonitrobenzenes, but 2-aminonaphthalene-1-thiol has not been prepared so far and consequently 7*H*-benzo[*c*]phenothiazines have not been prepared. In the present investigation preparation of 2-aminonaphthalene-1-thiol and its conversion into 8-nitro-7*H*-benzo[*c*]phenothiazine are reported. The synthetic route is as follows:



Schematic reaction.

Experimental

2-Aminonaphthalene-1-thiol was prepared by reacting β-naphthylamine (57.2 g, 0.4 mol) with Br_2 (80 ml) in 200 m of CH_3COOH and NH_4CNS (60.85 g) in 1 l of CH_3COOH and then refluxing 2-aminonaphtho(2′, 1′,: 4, 5)thiazole[4] thus formed with NaOH (550 g in 600 ml of H_2O) for 20 h. The reaction mixture was cooled, diluted with water (750 ml), filtered and neutralized with 5M-acetic acid. It was crystallized from ethanol as yellow crystals, mp 110 °C, yield 10 g (20%). Found: C, 68.50; H, 5.11; N, 7.97%, Calcd for $C_{10}H_9NS$: C, 68.57; H, 5.14; N, 8.00%. IR (KBr) 3330, 3510 (NH_2), and 2600 cm^{-1} (SH). 2-Aminonaphthalene-1-thiol (3.5 g, 0.02 mol) in 40 ml C_2H_5OH was converted into its sodium salt by refluxing with sodium hydroxide (0.8 g, 0.02 mol) in 10 ml H_2O and 20 ml of C_2H_5OH for five minutes. Sodium salt thus obtained was allowed to react with alcoholic solution of 2,6-dinitrochlorobenzene (4.0 g, 0.02 mol). The mixture was refluxed for 4 h and the product was crystallized from benzene–acetone mixture as violet crystals, mp 177 °C, yield 3.2 g (55%). IR (KBr) 3350 (NH), 1350, and 1500 cm^{-1} (NO_2). Found: C, 65.25; H, 3.38; N, 9.51%, Calcd for $C_{16}H_{10}N_2O_2S$: C, 65.30; H, 3.40; N, 9.52%.

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