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# SYNTHESES OF 5,6-DIAMINO-1,3-DIHYDRO-BENZO[*c*]THIOPHENE 2,2-DIOXIDE

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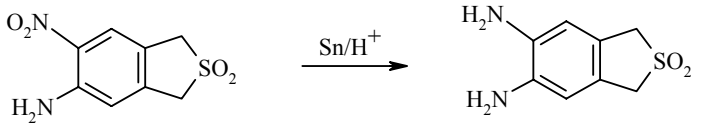
*5,6-Diamino-1,3-dihydrobenzo[c]thiophene 2,2-dioxide was obtained by two methods from 5-amino-6-nitro- and 5-acylamino-1,3-dihydrobenzo[c]thiophene 2,2-dioxide.*

**Keywords:** 5-amino-1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide, 5-amino-6-nitro-1,3-dihydrobenzo[*c*]-thiophene 2,2-dioxide, 5,6-diamino-1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide.

Aromatic and heterocyclic diamines are very reactive compounds and have been used successfully in the synthesis of derivatives of amines and other types of compounds. They are also used in the synthesis of heterocyclic compounds [1-3] and in the production of polymeric products [4].

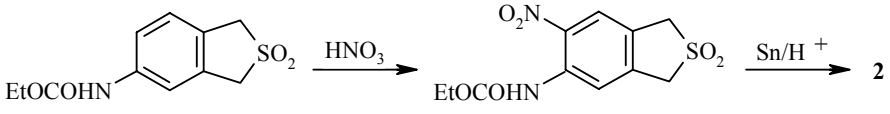
In this connection the synthesis and investigation of new aromatic and heterocyclic diamines and, in particular, such derivatives of 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide are extremely interesting.

Earlier [5] 5-amino-6-nitro-1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide (**1**) was synthesized from 5-amino-1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide in three stages by successive acylation, nitration, and hydrolysis of the acylaminonitro derivative.




**1** **2**

In the present work we reduced this nitroamino derivative with tin in hydrochloric acid and obtained the diamine **2** with a yield of 60%. However, it proved preparatively more convenient to start from the 5-ethoxycarbonylamino derivative **3**, the nitration of which with a nitrating mixture gave a good yield of 6-ethoxycarbonylamino-5-nitro-1,3-dihydrobenzo[*c*]thiophene 2,2-dioxide (**4**). During its reduction with tin in an acidic medium hydrolysis of the acylamino group took place at the same time, and a good yield of the diamine **2** was obtained.




**3** **4**

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## EXPERIMENTAL

The IR spectra of the synthesized compounds were recorded on a UR-20 spectrometer in tablets with potassium bromide. The $^1$H NMR spectra were obtained on a Tesla BS-487 spectrometer (80 MHz) with HMDS as internal standard. The melting points were determined on a Boetius microheater bench.

**5-Amino-6-nitro-1,3-dihydrobenzo[*c*]thiophene 2,2-Dioxide (1).** This compound was obtained by the method in [5].

**5,6-Diamino-1,3-dihydrobenzo[*c*]thiophene 2,2-Dioxide (2).** A. To a boiling mixture of the aminonitro compound **1** (456 mg, 2 mmol) and tin (400 mg) in ethanol (10 ml) concentrated hydrochloric acid (10 ml) was added dropwise. The mixture was boiled for a further 3 h, cooled, neutralized, and extracted with benzene. The solvent was distilled, and the residue was recrystallized from ethanol. The yield of the diamine was 240 mg (60.6%); mp 216-218°C. IR spectrum, ν, cm$^{-1}$: 1130, 1320 ($SO_2$); 3490 ($NH_2$). $^1$H NMR spectrum, δ, ppm: 4.30 (4H, s, $CH_2$); 5.00 (4H, $NH_2$); 6.90 (2H, s, CH). Found, %: C 48.54; H 4.92; S 16.13. $C_8H_{10}N_2O_2S$. Calculated, %: C 48.48; H 5.05; S 16.16.

B. To a boiling mixture of the nitro compound **4** (600 mg, 2 mmol) in ethanol (6 ml) and tin (600 mg) in ethanol (6 ml) concentrated hydrochloric acid (4 ml) was added dropwise. The mixture was boiled for a further 3 h, the solvent was distilled, and the residue was neutralized, extracted with benzene, and dried. The solvent was distilled, and the residue was recrystallized from ethanol. The yield of the diamine was 257 mg (64.9%); mp 216-218°C.

**5-Ethoxycarbonylamino-1,3-dihydrobenzo[*c*]thiophene 2,2-Dioxide (3).** This compound was obtained by the method in [6].

**6-Ethoxycarbonylamino-5-nitro-1,3-dihydrobenzo[*c*]thiophene 2,2-Dioxide (4).** Compound **3** (510 mg, 2 mmol) was dissolved in concentrated sulfuric acid (2.5 ml), concentrated nitric acid (2 ml) was added, and the mixture stirred at room temperature. The mixture was poured into iced water, and the precipitate was filtered off, dried, and recrystallized from acetone. The yield of the nitrocarbamate was 420 mg (70%); mp 211-212°C. IR spectrum, ν, cm$^{-1}$: 1130, 1315 ($SO_2$); 1360, 1340 ($NO_2$); 1680 (CO–NH). Found, %: C 43.93; H 4.14; S 10.55. $C_{11}H_{12}N_2O_6S$. Calculated, %: C 44.00; H 4.00; S 10.67.

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