

A Convenient Synthesis of 1,2-Benzenedithiol

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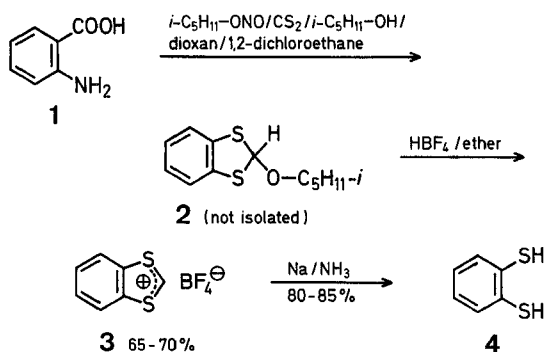
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The good results obtained in the conversion of functional groups with 1,3-benzoxathiolium salts¹ suggested the use of 1,3-benzodithiolium salts² in the same field of synthesis. 1,3-Benzodithiolium salts are usually prepared from 1,2-benzenedithiol³ (4) and we therefore needed large quantities of this latter compound.

Two useful methods are at present available, besides less convenient older methods⁴, for the preparation of 1,2-benzenedithiol:

- Conversion of 1,2-dibromobenzene to 1,2-bis[alkylthio]-benzenes followed by dealkylation⁵;
- Diazotization of 2-aminobenzenethiol, reaction of the resultant 1,2,3-benzothiadiazole with carbon disulfide in an autoclave, and hydrolysis of the 2-thioxo-1,3-benzodithiole thus obtained⁶.

Procedure (b) is the more convenient one but it is still rather laborious. In the present paper, we describe a new advantageous route to compound 4, according to the following scheme.



Anthranilic acid (1) is converted into 2-(3-methylbutoxy)-1,3-benzodithiole (2) according to the procedure of Nakayama⁷. The crude product 2 is treated with tetrafluoroboric acid-ether complex to give 1,3-benzodithiolium tetrafluoroborate (3) in good overall yield. The salt 3 is cleaved without difficulty by reduction with sodium in liquid ammonia.

1,3-Benzodithiolium Tetrafluoroborate (3):

A solution of anthranilic acid (1; 41.10 g, 0.30 mol) in dioxan (100 ml) is added, dropwise over a period of 1.5 h, to a stirred and gently refluxing solution of 3-methylbutyl nitrite (42.10 g, 0.36 mol), 3-methylbutanol (52.80 g, 0.60 mol), and carbon disulfide (150 ml) in 1,2-dichloroethane (800 ml), as described in Ref.⁷. The mixture is refluxed for 30 min, and part of the solvent and excess reagents are then distilled off under reduced pressure using a water bath at 50°. The residue (100–120 g) is dissolved in dry ether (400 ml), treated with charcoal, and filtered; then tetrafluoroboric acid/ether complex (50 ml) is added dropwise to the filtrate, with stirring and cooling. 1,3-Benzodithiolium tetrafluoroborate (3) precipitates immediately. It is isolated by filtration and washed several times with dry ether; yield (based on anthranilic acid): 46.8–50.4 g (65–70%); m.p. 154–155°, from acetonitrile/ether. The product can be stored protected from moisture and light but its immediate use is advisable.

The structure of 3 was confirmed by analytical data (C, H, S), and by the ¹H-N.M.R. spectrum in deuterio-trifluoroacetic acid, which was identical with that reported for 1,3-benzodithiolium perchlorate⁸.

1,2-Benzenedithiol (4):

A 1000 ml three-necked flask is equipped with an efficient dry ice/acetone condenser, a mechanical stirrer, and a gas-inlet tube. The flask is immersed in a dry ice/acetone bath, and a vigorous stream of dry ammonia is introduced into the system. When ~500–600 ml of liquid ammonia have been condensed, the gas-inlet tube is replaced by a stopper and the cooling bath is removed⁹. Then, 1,3-benzodithiolium tetrafluoroborate (3; 48 g, 0.20 mol) is rapidly introduced with stirring. While an ethanol bath is placed occasionally under the flask to ensure continuous boiling of the ammonia, sodium (16.10 g, 0.7 g-atom) is added in small pieces to the suspension, under vigorous stirring. Each piece of sodium must only be added after the former has been consumed. During the addition (~1.5 h), the solid reacts readily and the suspension becomes brown, then yellow, and then all the solid dissolves and the solution becomes brown and occasionally blue; a blue color persistent for almost 10 min indicates completion of the reaction. Stirring and cooling are stopped and the mixture is allowed to stand until the ammonia has evaporated. Then the residue is dissolved in ice water¹⁰, the solution extracted with ether, and the extract dried and evaporated. The residual oil is distilled under reduced pressure (b.p. 110–111°/12 torr), whereupon it solidifies spontaneously; yield: 22.7–24.1 g (80–85%); m.p. 27–28° (Ref.¹¹, m.p. 27–28°).

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- ⁹ Arrangements for cooling or condensing the ammonia can be made but are not necessary. The most simple method is to pass the liquid ammonia directly from a cylinder into the reaction flask.
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