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A CONVENIENT SYNTHESIS OF 1,3-BENZODITHIOLYLIUM FLUOROBORATE

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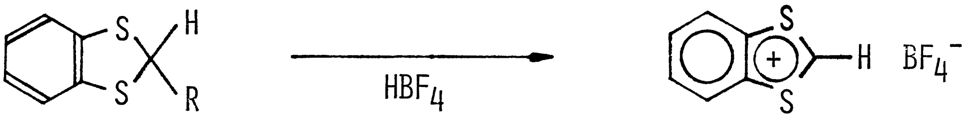
1,3-Benzodithiolylium fluoroborate (**I**) was synthesized in excellent yields by the action of hydrofluoroboric acid on 2-alkoxy- and 2-alkylthio-1,3-benzodithioles and by the action of trityl fluoroborate on 1,3-benzodithiole (**VI**). The fluoroborate **I** reacted with cycloheptatriene to give tropylium fluoroborate and **VI**.

The recent discovery of the highly conducting charge transfer salts of tetrathiafulvalenes with 7,7,8,8-tetracyanoquinonedimethane[1)] has prompted searches for the synthetic routes to 1,3-dithiolylium salts[2)] since they, on being treated with base, could give rise to tetrathiafulvalenes.[3)] Takamizawa and Hirai have reported that 2-methoxy-4-aryl-1,3-dithioles, which were prepared from 4-aryl-1,3-dithiolylium perchlorates and methanol, regenerated the original perchlorates by treatment with perchloric acid,[3b)] and more recently, Wudl et al. have synthesized 1,3-dithiolylium fluoroborate by the action of hydrofluoroboric acid on 2-methylthio-1,3-dithiole.[3f)] We wish to report a convenient synthesis of 1,3-benzodithiolylium fluoroborate (**I**), the benzo-analog of the parent 1,3-dithiolylium salt, by the action of hydrofluoroboric acid on 2-alkoxy- and 2-alkylthio-1,3-benzodithioles (**II** and **III**).

We have recently reported a one-step synthesis of 2-alkoxy-1,3-benzodithioles (**II**) on a preparative scale which involved addition of alcohols to 1,3-benzodithiol-2-ylidene produced from benzyne (generated by aprotic diazotization of anthranilic acid) and carbon disulfide.[4)] To a stirred and ice-cooled solution of 2-(3-methylbutoxy)-1,3-benzodithiole (**IIc**, 9.60g; 0.04 mol) in acetic anhydride (120 ml), 42% hydrofluoroboric acid (16.8g; 0.16 mol) was added dropwise during 20 min. After stirring at room temperature for 20 min, anhydrous ether (200 ml) was added to the mixture and the resulting precipitate was collected by filtration and washed with anhydrous ether (ca. 50 ml) to give 8.93g (93%) of 1,3-benzodithiolylium fluoroborate (I) as colorless crystals, mp 149-150°C (decomp.), δ (CF_3CO_2D) 8.06-8.26 and 8.66-8.86 (4H, AA'BB' m) and 11.50 (1H, s), ν_{max} 1000-1120 (BF_4^-) cm^{-1}, Found: C, 35.25; H, 2.11%, Calcd for $C_7H_5S_2BF_4$: C, 35.02; H, 2.10%. In similar ways, 2-methoxy- and 2-*n*-propoxy-1,3-benzodithioles (IIa and IIb) were converted into the fluoroborate I in a respective yield of 94% and 88%.

2-Alkylthio- and 2-arylthio-1,3-benzodithioles (III) have been easily obtained by the reaction of the dithiole IIc with thiols in acetic acid at room temperature.[5] 2-Ethylthio-, 2-cyclohexylthio-, and 2-phenylthio-1,3-benzodithioles (IIIa, IIIb, and IIIc) were also converted into the fluoroborate I in a respective yield of 86%, 90%, and 92% in a manner described above.

The only synthetic route available for preparing 1,3-benzodithiolylium salt has involved the condensation of *o*-benzenedithiol with formic acid in the presence of perchloric acid.[3h,3i,3j,6] However, the synthesis of the starting material, *o*-benzenedithiol, is considerably troublesome.[7] Thus, the new method is far more convenient than the literature method from the following points of view; a) the starting material is quite easily obtained by one-step synthesis, b) the reaction procedure is very simple and an analytically pure sample can be obtained in an excellent yield without further purification, c) the reaction is general with the both dithioles II and III, and d) the fluoroborate I is non-explosive, although 1,3-benzodithiolylium perchlorate explodes on being heated at its melting point.[3h,3i,3j]

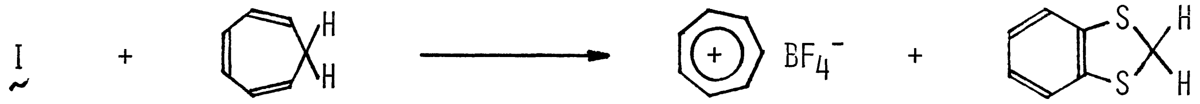


(I)

(IIa) ; R = OCH_3 (IIb) ; R = $O(CH_2)_2CH_3$
(IIc) ; R = $O(CH_2)_2CH(CH_3)_2$
(IIIa) ; R = SCH_2CH_3 (IIIb) ; R = S-*c*-C_6H_{11}
(IIIc) ; R = SC_6H_5

Hirai has reported that the reaction of 4-phenyl-1,3-dithiolylium perchlorate with a slight excess of cycloheptatriene (IV) in acetic acid at 80°C gave a mixture of tropylium perchlorate and the starting perchlorate.[8] However, the reaction of the fluoroborate I (15 mmol) with a slight excess of IV (17 mmol) in acetonitrile at 0°C resulted in the formation of tropylium fluoroborate (V, 90%), mp > 210°C (decomp.) [lit.[9] mp > 210°C (decomp.)] in addition to 1,3-benzodithiole (VI, 65%), bp 85-86°C/0.5mmHg (lit.[10] bp 88°C/0.6mmHg). This indicates that the positive charge of I, carrying a fused benzene ring, is more localized on the carbon at the 2-position compared with that of the parent 1,3-dithiolylium salt and hence, in ability to accept a hydride, I surpasses the parent 1,3-dithiolylium salt. In certain cases, therefore, I would be expected to serve as a hydride acceptor instead of trityl salt.

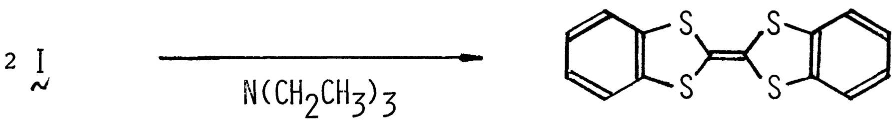
Next, 1,3-benzodithiole (VI) (obtained by the reaction described above) was allowed to react with trityl fluoroborate (VII) in acetonitirile at 0°C to give the fluoroborate I (75%) and triphenylmethane (VIII, 75%). The reaction provides another new synthetic route to I since the dithiole VI can be also obtained by the literature method.[10] These results lead to the conclusion that the ease of loss of a hydride, i.e., the stability of the resulting carbonium ions follows the order IV > VI > VIII.



(IV) (V) (VI)

$$\mathrm{VI} + \underset{(\mathrm{VII})}{(C_6H_5)_3C^+\ BF_4^-} \longrightarrow \mathrm{I} + \underset{(\mathrm{VIII})}{(C_6H_5)_3C\text{-}H}$$

Treating the fluoroborate I (10 mmol) with triethylamine (3 ml) in anhydrous acetonitrile (20 ml) at 0°C afforded dibenzotetrathiafulvalene (IX), mp 235-236°C (lit.[11] mp 235-236°C) in 81% yield in agreement with the finding with 1,3-benzodithiolylium perchlorate.[3h,3i,3j] Thus, the reaction sequence (II → I → IX) promises the most straightforward way to IX.[12] The physical and chemical properties of IX are of considerable interest.[13]



(IX)

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12) The tetrathiafulvalene IX has been also prepared by the thermal decomposition of the dithioles II.11) In this reaction, however, the yield of IX was low to moderate because of the formation of by-products.

13) The tetrathiafulvalene IX forms stable charge transfer salts with TCNQ, TCNE, DDQ, and the like (J. Nakayama, unpublished result). See also ref. 3i.

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