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A Convenient Synthesis of 2-Deuterio-1,3-benzodithiolylium Salts. Useful Synthon for the Preparation of One-carbon Homologated 1-Deuterio Aldehydes

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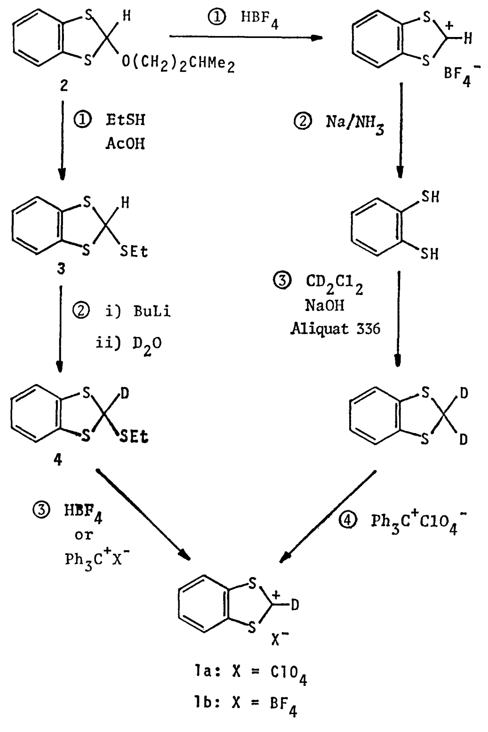
Synopsis. 2-Deuterio-1,3-benzodithiolylium salt, a useful synthon for preparation of one-carbon homologated 1-deuterio aldehydes, can be prepared in excellent overall yield in three steps starting from easily accessible 2-isopentoxy-1,3-benzodithiole.

Very recently Degani *et al.*[1] have shown that 2-deuterio-1,3-benzodithiolylium perchlorate (**1a**) is a useful synthon for preparation of one-carbon homologated 1-deuterio aldehydes; it reacts with Grignard reagents yielding 2-alkyl- or 2-aryl-2-deuterio-1,3-benzodithioles, which in turn can be hydrolyzed to the corresponding 1-deuterio aldehydes. However, the reported method for the preparation of **1a** is not so favorable since it requires even four steps, though starting from easily accessible 2-isopentyloxy-1,3-benzodithiole (**2**),[2,3] and expensive CD_2Cl_2 (Scheme 1).

We wish to report a simple three-step synthesis of 2-deuterio-1,3-benzodithiolylium salts (**1**) from **2**. In the new method, 2-ethylthio-1,3-benzodithiole (**3**), readily obtainable from **2** and ethanethiol,[4] is deuterated[5] and the resulting 2-deuterio-2-ethylthio-1,3-benzodithiole (**4**) is converted to 2-deuterio-1,3-benzodithiolylium tetrafluoroborate (**1b**) by treatment with tetrafluoroboric acid in 79% overall yield.[6] The isotopic purity of **1b** is over 98%; the small loss of isotopic purity observed may result from a deuterium-hydrogen exchange reaction of the 1,3-benzodithiolylium ion.[7]



Scheme 1.

More isotopically pure **1** can be obtained by treatment of **4** with a trityl salt in aprotic medium, where no deuterium-hydrogen exchange reaction occurs. Thus treatment of **4** with trityl perchlorate in acetonitrile gives isotopically pure **1a** and ethyl trityl sulfide in excellent yield. In a similar way, isotopically pure **1b** can be prepared from **4** and trityl tetrafluoroborate in good yield.[8]

Accordingly, the procedure developed here, which requires neither the laborious ring-cleavage step on the dithiole skeleton (Birch reduction) nor any expensive reagents, is far more convenient than that reported by Degani *et al.*[1]

Experimental

Caution. 1,3-Benzodithiolylium perchlorate explodes violently at its melting point; see *Tetrahedron Lett.*, **22**, pp. i—ii, 1981. The fluoroborate salt is nonexplosive and chemically behaves similarly to the perchlorate salt, and therefore the use of **1b** instead of **1a** should highly be recommended.

2-Ethylthio-1,3-benzodithiole (3). A mixture of **2**[3] (24.0 g; 0.1 mol) and ethanethiol (25 ml; 0.34 mol) in acetic acid (300 ml) was allowed to stand at room temperature overnight and then diluted with ice-water (1000 ml). The resulting crystalline white solid was collected and washed with 40% aqueous methanol (150 ml). The material was thoroughly dried to give **3** of sufficient purity (20.6 g, 96%): mp 45—46 °C (lit,[4] mp 50—51 °C).

2-Deuterio-2-ethylthio-1,3-benzodithiole (4). To a stirred solution of **3** (20.5 g; 95 mmol) in dry tetrahydrofuran (420 ml) was added dropwise a 15% solution of butyllithium in hexane (90 ml; 120 mmol) at −73 °C under nitrogen. The mixture was stirred for 2 h and then 6 ml of deuterium oxide (E. Merck, D content>99.75%) dissolved in dry tetrahydrofuran (40 ml) was added at −73 °C. After being stirred for 1 h at −73 °C, the mixture was gradually warmed to room temperature and evaporated. The residue was partitioned between ether (300 ml) and water (200 ml). The ether layer was washed with water and dried. The ether was removed to leave 20.1 g (97%) of **4** which is sufficiently pure for the preparation of **1** and used without further purification (no absorption due to the proton at C-2 could be detected by ^{1}H NMR analysis).

2-Deuterio-1,3-benzodithiolylium Tetrafluoroborate (1b). To a stirred and ice-cooled solution of **4** (20.1 g; 93 mmol) in acetic anhydride (250 ml) was added dropwise 42% tetrafluoroboric acid (40 g; 0.19 mol) over a period of 0.6 h. After completion of the addition, ether (300 ml) was added to the mixture to precipitate the product completely. The precipitate was collected by filtration and washed with ether to give 19.0 g (85%) of **1b**, mp 148—149 °C [lit,[6] mp of the unlabeled compound, mp 150—150.5 °C (decomp)]: IR (KBr) 2300 and 2250 (C-D) and 1000—1100 cm^{-1} (BF_4^-); ^{1}H NMR (CF_3CO_2D) δ=8.0—8.4 and 8.6—9.0 (4H, AA′BB′) (the content of the unlabeled compound was estimated to be less than 2% from the very weak absorption due to the proton at C-2 of the unlabeled compound which appears at $\delta=11.53$).[9]

*2-Deuterio-1,3-benzodithiolylium Salts (1) from **4** and Trityl Salts.* **4** (2.15 g; 10 mmol) was added to a stirred suspension of trityl perchlorate (3.60 g; 10.5 mmol) in dry acetonitrile (20 ml) cooled at −10 °C. The mixture was gradually warmed to room temperature, stirred for 0.5 h, and diluted with dry ether (50 ml). The solid prepcipitate was collected and washed with ether to give 2.28 g (90%) of isotopically pure **1a** in white crystal, which will explode at 185 °C (lit,[1] explosion point 182 °C). From the filtrate, 2.80 g (92%) of ethyl trityl sulfide, mp 117—118 °C, was obtained.

A similar treatment of **4** (10 mmol) with trityl tetrafluoroborate (10.5 mmol) in acetonitrile gave **1b** in 80% yield.

References

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2) I. Degani and R. Fochi, *Synthesis*, **1976**, 471.

3) J. Nakayama, *Synthesis*, **1975**, 38.

4) J. Nakayama, *Synthesis*, **1975**, 436.

5) Deuteration of **2** cannot be attained since butyllithium reacts with **2** to give 2-butyl-1,3-benzodithiole in a good yield; S. Ncube, A. Pelter, and K. Smith, *Tetrahedron Lett.*, **1977**, 255.

6) J. Nakayama, K. Fujiwara, and M. Hoshino, *Bull. Chem. Soc. Jpn.*, **49**, 3567 (1976).

7) For the hydrogen-deuterium exchange reaction of 1,3-dithiolylium ions, see H. Prinzbach and E. Futterer, *Adv. Heterocycl. Chem.*, **7**, 39 (1966).

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9) For ^{1}H NMR spectrum of the unlabeled compound, see K. Sakamoto, N. Nakamura, M. Ōki, J. Nakayama, and M. Hoshino, *Chem. Lett.*, **1977**, 1133.