Pentaatomic Heteroaromatic Cations; IX[1]. Preparation of 2-Substituted 1,3-Benzodithiolium Tetrafluoroborates as Useful Synthetic Intermediates from Esters

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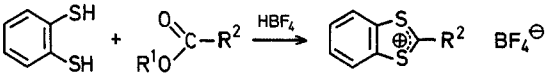
We have recently found that the well-known 1,3-benzodithiolium salts[2] are useful key intermediates in the conversion of some functional groups. Indeed, these salts are readily obtainable from carboxylic acids[2], acyl halides[2], aldehydes[1], and halides[3] and can be converted to aldehydes[3], aldehydes-1-*d*[1], ketones[3], and hydrocarbons[4] in high yields under mild conditions.

As a further extension of the previous studies, in the present communication we report the preparation of 2-substituted 1,3-benzodithiolium tetrafluoroborates from methyl and phenyl esters of aliphatic and aromatic carboxylic acids.



1 2 3

The pure salts were simply obtained by reaction of esters **2** with the now readily available 1,2-benzenedithiol (**1**)[5] in tetrafluoroboric acid/ether complex at 105–110° for 5–10 min.

Table. 2-Substituted 1,3-Benzodithiolium Tetrafluoroborates **3** from Esters **2**

Compound	R^2	Yield [%][a] **2**→**3** (R^1)	m.p.[b]	Molecular formula[c]	^{1}H-N.M.R.[d] δ [ppm]	U.V.[e] λ [nm] (log ε)
3a	*n*-C_3H_7	80 (CH_3) 85 (C_6H_5)	95–97°	$C_{10}H_{11}BF_4S_2$ (282.2)	1.24 (t, 3H, —$CH_2CH_2CH_3$, J=7.1 Hz), 2.23 (m, —$CH_2CH_2CH_3$), 3.90 (t, —$CH_2CH_2CH_3$, J=7.3 Hz), 7.98–8.32 + 8.60–8.92 (2 m, 4H_{arom})	253 f (3.71), 257 sh (3.83), 258 (3.85), 262 (3.86), 314 (3.87), 335 sh (3.64)
3b	*t*-C_4H_9	96 (CH_3) 100 (C_6H_5)	195–196°	$C_{11}H_{13}BF_4S_2$ (296.2)	1.94 (s, 9H, *t*-C_4H_9), 8.09–8.39 + 8.62–8.95 (2 m, 4H_{arom})	253 f (3.72), 257 sh (3.84), 258 (3.86), 262 (3.88), 314 (3.88), 335 sh (3.66)
3c	*n*-$C_{15}H_{31}$	97 (CH_3) 97 (C_6H_5) 94[g]	63–65°[f]	$C_{22}H_{35}BF_4S_2$ (450.2)	0.75–2.40 (m, 29H, *n*-$C_{14}H_{29}$), 3.90 (t, 2H, —CH_2—$C_{14}H_{29}$-*n*, J=7.5 Hz), 8.00–8.35 + 8.56–8.88 (2 m, 4H_{arom})	253 f (3.69), 257 sh (3.82), 258 (3.84), 262 (3.85), 314 (3.88), 335 sh (3.66)
3d	*cyclo*-C_6H_{11}	90 (CH_3) 96 (C_6H_5)	67–69°	$C_{13}H_{15}BF_4S_2$ (322.2)	1.20–2.90 (m, 10H, —$(CH_2)_5$—), 3.72–4.20 (m, 1H, >CH—), 8.05–8.42 + 8.62–8.98 (2 m, 4H_{arom})	253 f (3.73), 257 sh (3.85), 258 (3.86), 262 (3.88), 314 (3.89), 335 sh (3.71)
3e	C_6H_5	55[h] (CH_3) 100 (C_6H_5)	187–188°	$C_{13}H_9BF_4S_2$ (316.2)	7.85–8.55 (m, 7H_{arom}), 8.60–8.95 (m, 2H_{arom})	247 sh (3.67), 290 (3.66), 389 (4.39)
3f	4-H_3C—C_6H_4	77[h] (CH_3) 100 (C_6H_5)	167–168°	$C_{14}H_{11}BF_4S_2$ (330.2)	2.57 (s, 3H, CH_3), 7.60–7.85 (m, 2H_{arom}), 8.00–8.48 (m, 4H_{arom}), 8.50–8.90 (m, 2H_{arom})	250 sh (3.69), 296 (3.46), 408 (4.52)
3g	4-H_3CO—C_6H_4	92 (CH_3) 100 (C_6H_5)	263–264°	$C_{14}H_{11}BF_4OS_2$ (346.2)	4.15 (s, 3H, OCH_3), 7.29–7.55 (m, 2H_{arom}), 8.01–8.28 (m, 2H_{arom}), 8.30–8.75 (m, 4H_{arom})	260 sh (3.58), 299 (3.39), 4.28 (4.50)
3h	4-Cl—C_6H_4	30[h] (CH_3) 95 (C_6H_5)	236–237°	$C_{13}H_8BClF_4S_2$ (349.6)	7.70–8.60 (m, 6H_{arom}), 8.62–8.98 (m, 2H_{arom})	250 sh (3.69), 298 (3.55), 401 (4.47)

[a] Yield of pure, isolated product.

[b] Melting is always preceded by decomposition. The data reported refer to the temperature at which final melting took place. Unless otherwise noted, the tetrafluoroborates **3** were recrystallized from acetonitrile/ether and a few drops of tetrafluoroboric acid.

[c] All compounds gave satisfactory elemental microanalyses (C ±0.20%, H ±0.12%, S ±0.16%).

[d] The N.M.R. spectra were recorded in CF_3COOD with a Jeol INM-MH-60, using TMS as internal standard.

[e] Determined on a Beckman DB-G spectrometer. The solutions were made by dissolving salts **3** in 1 ml of acetonitrile (containing 2% of H_2SO_4 96%) and then diluted with H_2SO_4 under cooling. In this way the U.V. spectra are always reproducible and identical to those of the corresponding perchlorates in the same solvent (unpublished data). In contrast, the solutions of salts **3** directly in H_2SO_4 96% did not give reproducible data.

[f] Recrystallized from benzene/acetonitrile (1:1)-ether and a few drops of tetrafluoroboric acid.

[g] 30 mmol of 1,2-benzenedithiol and 30 ml of tetrafluoroboric acid/ether complex were used for 10 mmol of glyceride: R^1 = $-CH_2-CH(O-CO-C_{15}H_{31}\text{-}n)-CH_2-O-CO-C_{15}H_{31}\text{-}n$

[h] In this case the reaction mixture must be heated at 105–110° until the red solution becomes brown (exactly 6 min); longer times afforded less pure products.

The yields (Table) from all phenyl esters and from aliphatic methyl esters were always excellent; on the other hand, those from aromatic methyl esters were significantly dependent on the substituent electronic effects, decreasing on substitution of electron-donating with electron-withdrawing groups. The procedure was also effective in the particularly interesting case of the preparation of 2-*n*-pentadecyl derivative (**3**; $R^2 = n\text{-}C_{15}H_{31}$) from the corresponding glyceride.

The reported method is perhaps the simplest for the preparation of 2-substituted 1,3-benzodithiolium salts; it moreover seems to open up a new easy route for the conversion of esters to other functional derivatives.

Methyl esters were commercial products (Fluka); phenyl esters, with the exception of phenyl benzoate (Fluka), were prepared from the appropriate acyl chloride, phenol, and magnesium in dry benzene, according to the general procedure of Spassow[6].

General Procedure for the Preparation of 2-Substituted 1,3-Benzodithiolium Tetrafluoroborates (3):

A mixture of 1,2-benzenedithiol[5] (**1**; 1.42 g, 10 mmol) and the appropriate ester **2** (10 mmol) in tetrafluoroboric acid/ether complex (10 ml; 57% in ether) is heated at 105–110° in an oil-bath for 5–10 min and then allowed to stand at room temperature until cool (15–20 min). Dry ether (20–25 ml) is added to precipitate **3**. When $R^2 = n\text{-}C_{15}H_{31}$, 4-$H_3CO$—$C_6H_4$, the precipitation begins spontaneously and at once; when R^2 = Alkyl, the precipitation is completed by cooling the mixture in a refrigerator for 10–15 min. Then the tetrafluoroborates **3** are gathered by filtration, washed several times with dry ether, and vacuum dried. U.V. analysis showed that crude **3** were 100% pure (see Table).

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[1] I. Degani, R. Fochi, *Synthesis* **1976**, 759.

[2] D. S. Breslow, H. Skolnik, in: *Multi-sulfur and Sulfur and Oxygen Five- and Six-membered Heterocycles*, A. Weissberger, Ed., Interscience Publishers, New York, 1966, Chapter 5; and references therein.
H. Prinzbach, E. Futterer, *Adv. Heterocycl. Chem.* **7**, 39 (1966); and references therein.
E. Campaigne, R. D. Hamilton, *Quart. Rep. Sulfur Chem.* **5**, 275 (1970); and references therein.
R. Wizinger, *Quart. Rep. Sulfur Chem.* **5**, 191 (1970); and references therein.

[3] I. Degani, R. Fochi, *J. Chem. Soc., Perkin Trans. 1* **1976**, 1886.

[4] I. Degani, R. Fochi, to be published.

[5] I. Degani, R. Fochi, *Synthesis* **1976**, 471.

[6] A. Spassow, *Ber. Dtsch. Chem. Ges.* **75**, 779 (1942).