

## 1,3-Dithiolan-2-ylum and 1,3-Dithian-2-ylum Tetrafluoroborates from Carboxylic Acids

JO KLAVENESS and KJELL UNDHEIM

Department of Chemistry, University of Oslo, Oslo 3, Norway

A general method is given for the synthesis of acylium synthons masked as 2-substituted-1,3-dithiolan-2-ylum and -1,3-dithian-2-ylum tetrafluoroborates; acid chlorides are reacted with the respective dithiol in ethereal tetrafluoroboric acid. Ready conversions of the salts into dithioacetals and ketene dithioacetals are described. In the mass spectrometer the salts either undergo a thermal redox process with radical formation or suffer deprotonation to yield the volatile species.

Organometallic derivatives of 1,3-dithiolanes and 1,3-dithianes are important sources of anionic carbon in organic synthesis.<sup>1</sup> As a source of cationic carbon, however, these heterocycles have been relatively little exploited. Triphenylmethyl tetrafluoroborate has been used to prepare the cation from 1,3-dithiane,<sup>2</sup> and also to prepare 2-*p*-tolyl-1,3-dithiolan-2-ylum tetrafluoroborate in low yield by the same procedure.<sup>3</sup> 1,3-Dithiolan-2-ylum tetrafluoroborate has been prepared by the reaction of 2-methylthio-1,3-dithiolane with tetrafluoroboric acid,<sup>4</sup> and very recently it was reported that 2-methyl-1,3-dithiolan-2-ylum and -1,3-dithian-2-ylum perchlorate are formed from the respective dithiol and acetic anhydride in the presence of perchloric acid.<sup>5</sup>

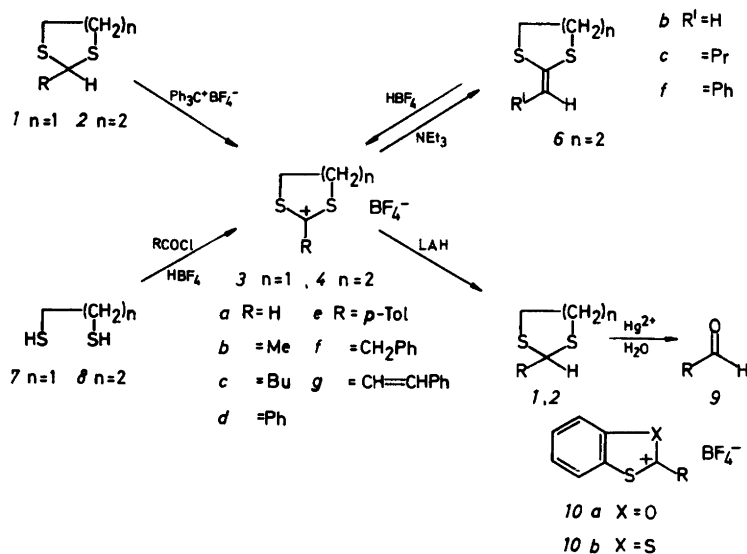
A carbenium ion which is stabilized by two adjacent heteroatoms, corresponds to a masked acylium ion. Because of the potential usefulness of such systems in organic synthesis, we became interested in developing routes for the preparation of 1,3-dithiolan-2-ylum **3** and 1,3-dithian-2-ylum **4** salts. In our first approach to the

synthesis of **4**, 2-methyl- (**2b**),<sup>6</sup> 2-benzyl- (**2f**)<sup>7</sup> and 2-phenyl-1,3-dithiane (**2d**)<sup>8</sup> were treated with triphenylmethyl tetrafluoroborate.<sup>9</sup> In agreement with other findings,<sup>10</sup> however, the yields of the dithianylum salts were unsatisfactory, although the parent compound **4a** is readily available by this method. The reaction is slow at room temperature, especially for the 2-phenyl derivative, and the increase in rate on heating is accompanied by decomposition of the thermolabile product.

In another approach for the synthesis of **4f**, 2-benzylidene-1,3-dithiane was treated with ethereal tetrafluoroboric acid to form the salt **4f**. The alkenyl derivatives **6** are available from the reaction between 2-lithium-2-trimethylsilyl-1,3-dithiane and aldehydes.<sup>11</sup> This approach excludes the preparation of salts in which the  $\alpha$ -carbon of the 2-substituent carries no hydrogen, e.g. the aryl derivatives (**3d**, **3e**, **4d**, **4e**). We have found, however, a general and a very simple method for the preparation of the salts **3** and **4** where the nature of simple 2-substituents does not impose restrictions on the reaction.

In the new approach **3** and **4** are formed in high yields from the respective dithiols and acid chlorides in ethereal tetrafluoroboric acid. The salts should be kept cold under anhydrous conditions, and most of them could be recrystallized from ether:acetonitrile on exclusion of moisture.

It would appear that the salts **3** and **4**, especially because they are readily available, are more useful as synthons than the 2-substituted benzo[1,3]oxatholium and benzo[1,3]ditholium tetrafluoroborates **10** which have been widely investigated for such purposes.<sup>12</sup>



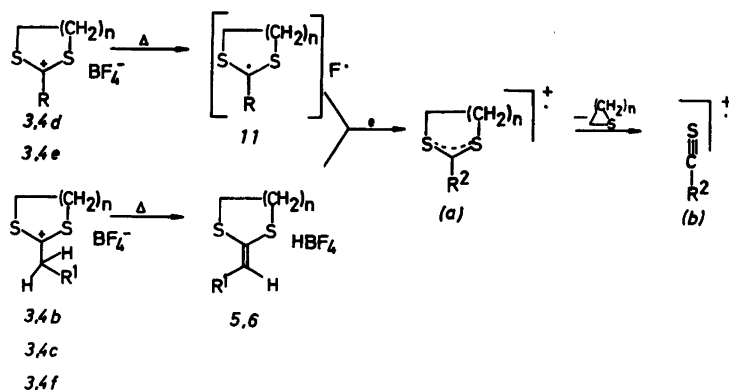
Scheme 1.

Reduction of 3 and 4 by lithium aluminium hydride in ether solution or by sodium borohydride in acetonitrile solution, gives the saturated heterocycles 1 and 2, respectively; the latter may be hydrolyzed to aldehyde or subjected to anionic reactions.

The salts 4b, 4c and 4f, in which the 2-substituent carries an  $\alpha$ -hydrogen, are readily deprotonated by triethylamine or by pyridine in acetonitrile solution to form the respective ketene thioacetals 6b, 6c and 6f.

The salts 3 and 4 are characterized by strong light adsorption; e.g. the long-wave band for the benzyl derivatives lies at 307 nm and the band undergoes a bathochromic shift with extended conjugation (3d, 3e) into the visible region with a band at 436 nm for the styryl derivative 3g. The cationic structures are further characterized by very low field  $^{13}C$ -shifts for C-2 which are in the region  $\delta$  190–249 ppm. The mass spectra of 3 and 4 fall into two major classes depending on the preferred reaction pathways before the volatile compounds from the salts can be generated; salts are not volatile because of the electrostatic attraction between the oppositely charged ions. The aryl derivatives 3d,e and 4d,e, however, show a strong molecular ion with mass number corresponding to the mass of the cation. By analogy to our previous findings for other stable cationic systems,<sup>13</sup> this observation can be

rationalized by a thermal redox process which occurs before volatilization generating the corresponding, volatile radical 11. From the latter, the cation (a) is regenerated in the gas phase on electron bombardment, (Scheme 2). The other major group of compounds (3f and 4b,c,f) are characterized by a molecular ion with mass number corresponding to the loss of a hydrogen from the cation. All these compounds have a hydrogen on the acyclic carbon adjacent to the cationic centre; the anion thus acts as a base and removes the hydrogen as a proton which results in the formation of alkyldene derivatives 5 and 6. The latter is the volatile species as we have demonstrated for related systems.<sup>13</sup> The styryl derivatives (3g and 4g) behave differently in that dimerization occurs to a large extent, after the primary redox process, and it is the dimeric products which are volatilized. A common feature in the fragmentation is the formation of a species corresponding to the side-chain which also includes C-2 and one of the sulfur atoms; the species is tentatively drawn as (b) in Scheme 2; this species is the base peak in some of the spectra. The neutral fragment expelled corresponds to a unit of thiirane or thietane. The fragmentation patterns compare with what have been published for 1,2-dithiolylium salts.<sup>14</sup>



Scheme 2.

## EXPERIMENTAL

The mass spectra of the salts were recorded by direct insertion into the ion source at 225 °C. The data are presented as MS [70 eV;  $m/z$  (% rel. int.)].

All the reactions were carried out under an atmosphere of dry argon. The ether used as solvent was dried over sodium, the acetonitrile was dried over  $\text{P}_2\text{O}_5$  before distillation and was then kept over molecular sieve (3 Å).

**1,3-Dithian-2-ylum tetrafluoroborate 2a** by *hydride abstraction*. 1,3-Dithiane<sup>15</sup> was reacted with triphenylmethyl tetrafluoroborate<sup>9</sup> as described except that acetonitrile was found to be a superior solvent for this reaction; yield 76 %.

**2-Substituted 1,3-dithiolan-2-ylum tetrafluoroborates from acid chlorides.** 54 %  $\text{HBF}_4$  in ether (5 ml) was added dropwise at 0 °C to a solution of the acid chloride (10 mmol) and ethane-1,2-dithiol (10 mmol) or propane-1,3-dithiol (10 mmol) in ether (50 ml). The mixture was stirred for 15 min at this temperature, stirred for another 10 min at room temperature and finally heated under reflux for 20 min. The precipitated product, after isolation, was triturated with ether for purification; an oily product crystallized during this treatment.

**2-Phenyl-1,3-dithiolan-2-ylum tetrafluoroborate 3d** was obtained in 83 % yield; yellow crystalline material from  $\text{MeCN-Et}_2\text{O-HBF}_4$  (drops), m.p. 100–103 °C.  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  4.35 ( $\text{CH}_2\text{CH}_2$ ), 7.3–8.2 (Ph).  $^{13}\text{C NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  44.7 ( $\text{CH}_2\text{CH}_2$ ), 130.8–140.9 (Ph), 232.7 (C-2). UV ( $\text{CH}_2\text{Cl}_2$ ): 348 (log  $\epsilon$  3.58), 235 nm (4.28). MS: 182 (6), 181 (36, M), 171 (7), 122 (9), 121 (100), 77 (40).

**2-(4-Tolyl)-1,3-dithiolan-2-ylum tetrafluoro-**

**borate 3e** was obtained in 88 % yield; yellow crystalline material from  $\text{MeCN-Et}_2\text{O-HBF}_4$  (drops), m.p. 117–120 °C.  $^1\text{H NMR}$  (TFA):  $\delta$  2.60 (Me), 4.40 ( $\text{CH}_2\text{CH}_2$ ), 7.3–7.5 and 7.9–8.1 (Ph).  $^{13}\text{C NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  21.9 (Me), 44.3 ( $\text{CH}_2\text{CH}_2$ ), 129.2–154.9 (Ph), 230.9 (C-2). UV ( $\text{CH}_2\text{Cl}_2$ ): 373 (log  $\epsilon$  4.32), 267 (3.42), 235 nm (3.68). MS: 195 (3), 194 (14, M), 136 (10), 135 (100), 91 (28), 65 (11).

**2-Benzyl-1,3-dithiolan-2-ylum tetrafluoroborate 3f** was obtained in 96 % yield; off-white crystalline material from  $\text{MeCN-Et}_2\text{O-HBF}_4$  (drops), m.p. 108–110 °C.  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  4.30 ( $\text{CH}_2\text{CH}_2$ ), 4.60 ( $\text{CH}_2$ ), 7.30 (Ph).  $^{13}\text{C NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  41.0 ( $\text{CH}_2$ ), 46.7 ( $\text{CH}_2\text{CH}_2$ ), 126.9–135.7 (Ph), 248.9 (C-2). UV ( $\text{CH}_2\text{Cl}_2$ ): 307 nm (log  $\epsilon$  4.29), MS: 195 (12, M), 194 (100), 166 (67), 134 (54), 122 (14), 121 (29), 90 (37), 89 (23).

**2- $\beta$ -Styryl-1,3-dithiolan-2-ylum tetrafluoroborate 3g** was obtained in 92 % yield; orange needles from  $\text{MeCN-Et}_2\text{O-HBF}_4$  (drops), m.p. 155–158 °C.  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  4.30 ( $\text{CH}_2\text{CH}_2$ ), 7.5–7.9 (Ph), 8.00 and 8.35 ( $\text{CH}=\text{CH}$ ,  $J_{\text{trans}}$  16 Hz).  $^{13}\text{C NMR}$  ( $\text{CD}_3\text{CN}$ ): 44.5 ( $\text{CH}_2\text{CH}_2$ ), 122.5 ( $\beta$ -CH), 132.8–136.4 (Ph), 157.4 ( $\alpha$ -CH), 225.7 (C-2). UV ( $\text{CH}_2\text{Cl}_2$ ): 436 (log  $\epsilon$  4.40), 244 nm (3.87). MS: 412 (100), 208 (43), 207 (12), 147 (37), 115 (24), 91 (18), 77 (13).

**2-Methyl-1,3-dithian-2-ylum tetrafluoroborate 4b** was obtained in 66 % yield as a yellow crystalline material which decomposed in contact with the atmosphere.  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  2.2–2.6 ( $\text{CH}_2$ -5), 2.90 (Me), 3.5–3.8 (2  $\text{CH}_2$ -4.6),  $^{13}\text{C NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  16.9 (C-5), 32.4 (Me), 33.6 (2 $\text{CH}_2$ -4.6), 229.4 (C-2). UV ( $\text{CH}_2\text{Cl}_2$ ): 310, 287 and 228 (log  $\epsilon$  not given because of rapid decomposition). MS: 134 (10),

133 (12, M), 132 (100, M-H), 99 (17), 90 (10), 85 (11), 74 (21).

**2-Butyl-1,3-dithian-2-ylum tetrafluoroborate 4c** was obtained in 82 % yield as a yellow oily material.  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  2.2–2.6 ( $\text{CH}_2$ -5), 3.5–3.8 ( $2\text{CH}_2$ -4.6), 3.2–3.4 and 1.0–2.1 (Bu).  $^{13}\text{C NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  16.7 (Me), 20.2, 25.3, 37.1, 49.4 ( $4\text{CH}_2$ ), 36.3 ( $2\text{CH}_2$ -4.6), 236.9 (C-2). UV ( $\text{CH}_2\text{Cl}_2$ ): 312 nm ( $\log \epsilon$  3.53). MS: 175 (3, M), 174 (27, M-H), 145 (100), 71 (51).

**2-Phenyl-1,3-dithian-2-ylum tetrafluoroborate 4d** was obtained in 87 % yield; white crystalline material from  $\text{MeCN-Et}_2\text{O-HBF}_4$  (drops), m.p. 188–191 °C.  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ ): 2.3–2.5 ( $\text{CH}_2$ -5), 3.6–3.8 ( $2\text{CH}_2$ -4.6), 7.4–8.0 (Ph).  $^{13}\text{C NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  18.2 ( $\text{CH}_2$ -5), 34.5 ( $2\text{CH}_2$ -4.6), 128.6–138.7 (Ph), 223.2 (C-2). UV ( $\text{CH}_2\text{Cl}_2$ ): 335 ( $\log \epsilon$  4.04), 266 (3.41), 236 nm (3.66). MS: 196 (17), 195 (95, M), 160 (13), 122 (16), 121 (100), 106 (12), 105 (48).

**2-(4-Tolyl)-1,3-dithian-2-ylum tetrafluoroborate 4e** was obtained in 72 % yield as a yellow oily material.  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  2.50 (Me), 2.4–2.7 ( $\text{CH}_2$ -5), 3.7–3.9 ( $2\text{CH}_2$ -4.6), 7.2–7.8 (Ph).  $^{13}\text{C NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  24.7 ( $\text{CH}_2$ -5), 25.1 (Me), 37.1 ( $2\text{CH}_2$ -4.6), 131.5–154.4 (Ph), 224.5 (C-2). UV ( $\text{CH}_2\text{Cl}_2$ ): 366 ( $\log \epsilon$  4.11), 276 (2.94), 242 nm (3.34). MS: 210 (5), 209 (17, M), 136 (12), 135 (98), 119 (100), 107 (21), 91 (38).

**2-Benzyl-1,3-dithian-2-ylum tetrafluoroborate 4f** was obtained in 70 % yield; white crystalline material, m.p. 94–97 °C.  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  2.1–2.5 ( $\text{CH}_2$ -5), 3.4–3.7 ( $2\text{CH}_2$ -4.6), 4.40 ( $\text{CH}_2$ ), 7.30 (Ph).  $^{13}\text{C NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  17.2 ( $\text{CH}_2$ -5), 33.8 ( $2\text{CH}_2$ -4.6), 51.4 ( $\text{CH}_2$ ), 130.0–134.8 (Ph), 233.0 (C-2). UV ( $\text{CH}_2\text{Cl}_2$ ): 334 ( $\log \epsilon$  3.89), 309 nm (4.19). MS: 209 (13, M), 208 (100, M-H), 161 (7), 135 (10), 134 (99), 91 (10), 90 (13), 88 (11).

**2- $\beta$ -Styryl-1,3-dithian-2-ylum tetrafluoroborate 4g** was obtained in 93 % yield; yellow crystalline material, m.p. 126–127 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 2.3–2.5 ( $\text{CH}_2$ -5), 3.5–3.8 ( $2\text{CH}_2$ -4.6), 7.4–7.8 (Ph-CH=), 8.05 (CH=,  $J_{\text{trans}}$  16 Hz).  $^{13}\text{C NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  18.9 (C-5), 32.9 ( $2\text{CH}_2$ -4.6), 128.0–134.8 (PhCH=), 147.8 (CH=), 215 (C-2). UV ( $\text{CH}_2\text{Cl}_2$ ): 431 ( $\log \epsilon$  3.49), 303 nm (4.43). MS: 222 (4), 221 (6, M), 147 (100), 117 (9).

**2-Benzyl-1,3-dithian-2-ylum tetrafluoroborate 4f** by protonation of 6f. 54 %  $\text{HBF}_4$  in ether (3 ml) was added dropwise with stirring at 0 °C to a solution of 2-benzylidene-1,3-dithiane <sup>11</sup> in ether (30 ml). After the addition was complete, the mixture was allowed to reach room temperature and the separated solid triturated with ether; yield 74 %.

**1,3-Dithianes 2 by reduction of the salts 4. LAH reduction.** Lithium aluminium hydride (12 mmol)

was added to a suspension of the salt (10 ml) in ether (30 ml) and the mixture stirred for 2 min before it was poured into saturated aqueous  $\text{NH}_4\text{Cl}$  solution. The organic layer was separated, the aqueous phase extracted with ether, the combined ether solutions dried ( $\text{MgSO}_4$ ), the ether distilled off, and the residue purified either by distillation or by recrystallization.

**2-Methyl-1,3-dithiane <sup>6</sup> 2b**, b.p. 66 °C/5 mmHg; yield 64 %.

**2-Butyl-1,3-dithiane <sup>16</sup> 2c**, b.p. 88–90 °C/0.6 mmHg; yield 82 %.

**2-Phenyl-1,3-dithiane <sup>8</sup> 2d**, m.p. 68–70 °C; yield 97 %.

**2-Benzyl-1,3-dithiane <sup>7</sup> 2f**, b.p. 120–121 °C/0.3 mmHg; yield 84 %.

**Sodium borohydride reduction.** Sodium borohydride (9 mmol) was added with stirring at 0 °C to a solution of the salt (8 mmol) in acetonitrile (30 ml). The mixture was stirred for 30 min after the addition was completed, and the reaction mixture worked up as under the LAH-reduction.

**2-Phenyl-1,3-dithiane <sup>8</sup> 2d**, m.p. 68–70 °C (MeOH); yield 86 %.

**2-(4-Tolyl)-1,3-dithiane <sup>17</sup> 2e**, m.p. 82–83 °C (light petroleum); yield 72 %.

**2-Alkylidene-1,3-dithianes 6.** Triethylamine (15 mmol) in acetonitrile (5 ml) was added dropwise to a solution of the 1,3-dithian-2-ylum tetrafluoroborate (10 mmol) in acetonitrile (25 ml) at 0 °C. The mixture was stirred for 5 min at this temperature before it was allowed to warm up to room temperature. The solvent was then allowed to distill off at reduced pressure, the residue extracted with chloroform ( $3 \times 100$  ml), the dried ( $\text{MgSO}_4$ ) solution evaporated and the residue distilled.

**2-Methylen-1,3-dithiane <sup>11</sup> 6b**, b.p. 78–80 °C/8 mmHg; yield 74 %.

**2-Butylidene-1,3-dithiane <sup>18</sup> 6c**, b.p. 68–70 °C/0.08 mmHg; yield 88 %.

**2-Benzylidene-1,3-dithiane <sup>11</sup> 6f**, b.p. 120–122 °C/0.05 mmHg; yield 93 %.

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