

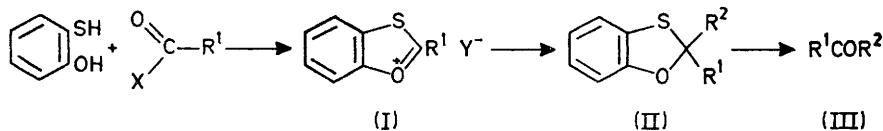
## Pentatomic Heteroaromatic Cations. Part V.<sup>1</sup> A Convenient General Method for the Preparation of Aldehydes from Acyl Chlorides *via* 2-Substituted 1,3-Benzoxathiolium Tetrafluoroborates

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Reactions at 35 °C of acyl chlorides with *o*-mercaptophenol in tetrafluoroboric acid–ether or boron trifluoride–ether complex gave excellent yields of the corresponding 2-substituted 1,3-benzoxathiolium tetrafluoroborates. Reduction of the products with sodium borohydride (or sodium borodeuteride) in acetonitrile at 0–20 °C gave 2-substituted 1,3-benzoxathioles. These were hydrolysed with mercury(II) chloride to the corresponding aldehydes. Overall yields were equally good (70–90%) in the preparation of aliphatic, alicyclic, and aromatic aldehydes.

OUR previous work<sup>1–4</sup> has shown that 2-substituted 1,3-benzoxathiolium salts act as useful intermediates for the conversion of carboxylic acids into aldehydes and ketones (Scheme; X = OH, Y = ClO<sub>4</sub>). We now

High yields of 2-substituted 1,3-benzoxathiolium tetrafluoroborates (I; Y = BF<sub>4</sub>) could be obtained by reaction at 35 °C of acyl chlorides with *o*-mercaptophenol in either tetrafluoroboric acid–ether or boron trifluoride–



SCHEME

report an investigation of the conversion of acyl chlorides into carbonyl compounds *via* 2-substituted 1,3-benzoxathiolium salts.

<sup>1</sup> Part IV, I. Degani, R. Fochi, and P. Tundo, *Gazzetta*, 1975, **105**, 907.

<sup>2</sup> I. Degani, R. Fochi, and P. Tundo, *J. Heterocyclic Chem.*, 1974, **11**, 507.

ether complex (Table I). As expected, the conditions required were milder than those for conversion of the

<sup>3</sup> L. Costa, I. Degani, R. Fochi, and P. Tundo, *J. Heterocyclic Chem.*, 1974, **11**, 943.

<sup>4</sup> I. Degani, R. Fochi, and P. Tundo, Communication at the VIIIth Convegno di Chimica Organica, Siena, Italy, September 23–27, 1974, Abstracts p. 71.

corresponding carboxylic acids.<sup>3,5</sup> The tetrafluoroborates were readily isolated in a high degree of purity. Although they were more sensitive to air than perchlorates, they could nevertheless be stored cold and dry for several months without appreciable alteration. Their handling, even on a large scale, was free of the risks associated with perchlorates. Their structures were confirmed by elemental analysis † and spectroscopic data (n.m.r. in  $\text{CF}_3\text{-CO}_2\text{D} \ddagger$ ).

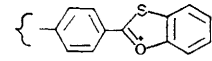
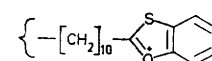
Reduction to the corresponding 2-substituted 1,3-benzoxathioles (II;  $\text{R}^2 = \text{H}$ ) was readily performed in

more important general methods.<sup>6a,b</sup> The main advantages of the new method are (i) that it appears to be equally satisfactory in aliphatic, alicyclic, and aromatic series, (ii) its simplicity, and (iii) the high degree of purity of the aldehydes obtained.

2-Substituted 1,3-benzoxathiole tetrafluoroborates are, like the analogous perchlorates<sup>1-4</sup> potential intermediates for the synthesis of ketones (III;  $\text{R}^1$  and  $\text{R}^2 = \text{alkyl or aryl}$ ). Test reactions, however, have shown that complete reaction with Grignard reagents to give 2,2-disubstituted 1,3-benzoxathioles (II;  $\text{R}^1$  and

TABLE I

2-Substituted 1,3-benzoxathiole tetrafluoroborates (I;  $\text{Y} = \text{BF}_4$ )

$\text{R}^1$	Yield (%)	Time <sup>a</sup> (h)	M.p. (°C) <sup>b</sup>	U.v. data <sup>c</sup> $\lambda/\text{nm}$ (log $\epsilon$ )
Ph	91 <sup>d</sup>	24	204—205 <sup>g</sup>	<i>e</i>
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	93 <sup>d</sup>	24	238—240	<i>e</i>
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	94 <sup>d</sup>	24	218—220	<i>e</i>
<i>o</i> -ClC <sub>6</sub> H <sub>4</sub>	90 <sup>d</sup>	24	177—179	236 (3.61), 275 (3.77), 373 (4.34)
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	95 <sup>d</sup>	24	210—212	<i>e</i>
<i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	96	24	176—178	<i>e</i>
<i>p</i> -EtO <sub>2</sub> C-C <sub>6</sub> H <sub>4</sub>	92	24	140—142	275 (4.17), 373 (4.31)
2-Naphthyl	92 <sup>d</sup>	2	209—211	248 (4.08), 261 (4.04), 278 (4.00), 293 (3.65), 398 (4.46), 430sh (4.18)
 $\text{BF}_4^-$	83	2	216—218 <sup>f</sup>	278 (4.10), 434 (4.55), 450sh (4.47)
Pr <sup>n</sup>	84	2	103—105	244sh (3.66), 247 (3.69), 252 (3.65), 298 (3.89)
Bu <sup>t</sup>	84	2	137—139	244sh (3.46), 248 (3.54), 252 (3.45), 300 (3.84)
n-C <sub>15</sub> H <sub>31</sub>	Quant.	2	67—69 <sup>g</sup>	244sh (3.47), 248 (3.54), 252 (3.45), 299 (3.85)
 $\text{BF}_4^-$	92	2	100—102 <sup>h</sup>	244sh (4.03), 248 (4.06), 252 (4.02), 299 (4.24)
Cyclohexyl	85	2	69—71	244sh (3.63), 248 (3.67), 252 (3.61), 300 (3.92)

<sup>a</sup> Reactions carried out at 35 °C. Higher temperatures give the same yields in shorter times. There is often a fall in purity, however. <sup>b</sup> Melting is always preceded by decomposition. The data reported (not always reproducible) refer to the temperature at which final melting took place. Unless otherwise noted, the tetrafluoroborates were recrystallized from acetonitrile-ether. <sup>c</sup> Determined on a Beckman DB-G spectrometer in 96% H<sub>2</sub>SO<sub>4</sub>. <sup>d</sup> Obtained in comparable yields also by using boron trifluoride-ether instead of tetrafluoroboric acid (same amounts, reaction times, and temperature). <sup>e</sup> Identical with those of the corresponding perchlorate in the same solvent. <sup>f</sup> Recrystallized from acetonitrile-ether and a few drops of tetrafluoroboric acid. <sup>g</sup> Recrystallized from benzene-ether and a few drops of tetrafluoroboric acid. <sup>h</sup> Recrystallized from acetonitrile-benzene. <sup>i</sup> Recrystallized from benzene-acetonitrile (1 : 1)-ether and a few drops of tetrafluoroboric acid.

high yield (Table 2) with sodium borohydride in acetonitrile at 0—20 °C. These intermediates were pure enough to be employed directly in the next stage.

When the tetrafluoroborate was obtained by the action of tetrafluoroboric acid, the reaction mixture could be reduced without isolation of the salt; the overall yields were unchanged.

Hydrolysis of the 2-substituted 1,3-benzoxathioles to the aldehydes (III;  $\text{R}^2 = \text{H}$ ) under the conditions reported elsewhere<sup>3</sup> raised no difficulties.

The method described here has the advantage of enabling deuterated aldehydes to be synthesised from acyl chlorides, *i.e. via* reduction of the tetrafluoroborates with sodium borodeuteride (Table 2, footnote *b*).

The overall yields from the conversion of acyl chlorides (Table 2) are at least comparable with those given by the

$\text{R}^2 = \text{alkyl or aryl}$ ) can only be achieved with the consumption of 4—5 mol of reagent per mol of tetrafluoroborate (an example is given in the Experimental section). Conversion of tetrafluoroborates into ketones thus appears to be convenient only in cases where large supplies of Grignard reagent are available.

On the other hand, tetrafluoroborates can be readily converted into perchlorates without excessive loss. Conversion of 2-phenyl-1,3-benzoxathiole tetrafluoroborate into the corresponding perchlorate, through 2-ethoxy-2-phenyl-1,3-benzoxathiole, for instance, proceeds in 90% yield.

#### EXPERIMENTAL

*General Method for the Preparation of 2-Substituted 1,3-Benzoxathiole Tetrafluoroborates* (I;  $\text{Y} = \text{BF}_4$ ,  $\text{R}^1 =$

<sup>a</sup> (a) R. C. Fuson, in 'The Chemistry of the Carbonyl Group,' ed. S. Patai, Interscience, New York, 1966, ch. 4 and references therein; (b) O. H. Wheeler, in 'The Chemistry of Acyl Halides,' ed. S. Patai, Interscience, New York, 1972, ch. 7 and references therein.

† Submitted to referees.

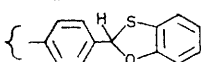
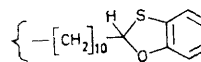
‡ Available on request from the authors.

<sup>5</sup> I. Degani, R. Fochi, and P. Tundo, *Ann. Chim. (Italy)*, 1972, **62**, 570.

*alkyl or aryl*).—A solution of *o*-mercaptophenol<sup>7</sup> (1.26 g, 0.01 mol) in tetrafluoroboric acid–ether (2.5 ml; 57% in ether) was cautiously added to an ice-cold solution of acyl chloride (0.01 mol) in the same solvent (2.5 ml). Precipitation of the tetrafluoroborate always begins at once ( $R^1 = \text{aryl}$ ). The mixture was left at 35°C (bath temp.) for 2 or 24

TABLE 2

Yields of 2-substituted 1,3-benzoxathioles (II;  $R^2 = \text{H}$ ) from tetrafluoroborates and overall yields of aldehydes (III;  $R^2 = \text{H}$ ) from the starting acyl chlorides

$R^1$	Yield (%) of (II; $R^2 = \text{H}$ )	Ref.	Overall yield (%) of $R^1\text{CHO}^a$
Ph <sup>b</sup>	96	2	87
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	97	3	87
<i>p</i> -MeO·C <sub>6</sub> H <sub>4</sub>	97	3	91
<i>o</i> -ClC <sub>6</sub> H <sub>4</sub>	96	3	84
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	95	3	88
<i>m</i> -NO <sub>2</sub> ·C <sub>6</sub> H <sub>4</sub>	94	3	79
<i>p</i> -EtO <sub>2</sub> C·C <sub>6</sub> H <sub>4</sub>	95	This work <sup>c</sup>	80 <sup>d</sup>
2-Naphthyl	97	3	81
	88 <sup>e</sup>	3	71
Pr <sup>iii</sup>	98	3	78
Bu <sup>t</sup>	98	3	81
n-C <sub>16</sub> H <sub>31</sub>	96	3	92
	98 <sup>e</sup>	This work <sup>f</sup>	88 <sup>d,h</sup>
Cyclohexyl	95	3	81

<sup>a</sup> Unless otherwise noted the yields of aldehydes from 2-substituted 1,3-benzoxathioles are taken from ref. 3. <sup>b</sup> The use of sodium borodeuteride produced in comparable yield the 2-deuterio-derivative (II;  $R^1 = \text{Ph}$ ,  $R^2 = \text{D}$ ).<sup>3</sup> Hydrolysis to afford the pure benz[<sup>2</sup>H]aldehyde has been reported.<sup>3</sup> <sup>c</sup> M.p. 37–38° (from methanol) (Found: C, 67.0; H, 4.95; S, 11.25. C<sub>16</sub>H<sub>14</sub>O<sub>2</sub>S requires C, 67.15; H, 4.9; S, 11.2%);  $\delta(\text{CDCl}_3)$  1.38 (t, CH<sub>3</sub>,  $J$  7.5 Hz), 4.41 (q, CH<sub>2</sub>,  $J$  7.5 Hz), 6.95–7.45 (5 H, m, aromatic and CH), and 7.68 and 8.17 (AB system, C<sub>6</sub>H<sub>4</sub>,  $J$  8.3 Hz). <sup>d</sup> For yield from 2-substituted 1,3-benzoxathiole see Experimental section. <sup>e</sup> Ratio of tetrafluoroborate to sodium borohydride 0.01 mol : 0.5 g. <sup>f</sup>  $R^1 = p\text{-OHC}\cdot\text{C}_6\text{H}_4$ . <sup>g</sup> M.p. 64–66° (from methanol) (Found: C, 69.65; H, 7.3; S, 15.5. C<sub>24</sub>H<sub>36</sub>O<sub>2</sub>S<sub>2</sub> requires C, 69.55; H, 7.25; S, 15.45%);  $\delta(\text{CF}_3\text{CO}_2\text{D})$  1.35 (m, 10 CH<sub>2</sub>), 6.10 (t, CH,  $J$  5.6 Hz), and 6.70–7.30 (4 H, m, aromatic). <sup>h</sup>  $R^1 \text{OCH}\cdot[\text{CH}_2]_{10}$ .

h. Then, after cooling, dry ether (10–15 ml) was added to complete the precipitation. For yields and physical data see Table 1.

In some cases boron trifluoride–etherate can be used instead of tetrafluoroboric acid (Table 1).

**General Method for the Preparation of 2-Substituted 1,3-Benzoxathioles (II;  $R^1 = \text{alkyl or aryl}$ ,  $R^2 = \text{H}$ ).** (A) Powdered sodium borohydride (0.25 g) was gradually added, over 10 min, to a stirred ice-cold solution of freshly prepared 2-substituted 1,3-benzoxathiolylium tetrafluoroborate (0.01 mol) in acetonitrile (30 ml) and a few drops of tetrafluoroboric acid–ether. Stirring was continued until the yellow colour disappeared (*ca.* 5–10 min). The solution was then poured into water and extracted with ether. The extract was washed with aqueous sodium hydroxide (5%) and

water, and then dried and evaporated to give the 2-substituted 1,3-benzoxathiole (II). Yields are reported in Table 2. Use of sodium borodeuteride produced the 2-deuterio-derivative in comparable yield (Table 2).

(B) The reaction mixture in tetrafluoroboric acid was left at 35°C as described above for the times indicated in Table 2. It was then directly diluted with acetonitrile (30 ml). After cooling with an ice-bath, powdered sodium borohydride (0.4 g) was gradually added over 10 min, with stirring. The 2-substituted 1,3-benzoxathiole (II) was obtained exactly as in (A), with the same overall yield and degree of purity.

**Ethyl *p*-Formylbenzoate (III;  $R^1 = p\text{-EtO}_2\text{C}\cdot\text{C}_6\text{H}_4$ ,  $R^2 = \text{H}$ ).**—2-(*p*-Ethoxycarbonylphenyl)-1,3-benzoxathiole (II;  $R^1 = p\text{-EtO}_2\text{C}\cdot\text{C}_6\text{H}_4$ ,  $R^2 = \text{H}$ ) (1.43 g, 0.005 mol) in dimethyl sulphoxide–water (18 ml; 5 : 1) was hydrolysed with mercury(II) chloride (4.07 g, 0.015 mol) by the procedure previously reported.<sup>3</sup> The reaction time was 30 min and the yield was 92%. The pure aldehyde obtained was identified by comparison with the authentic compound<sup>8</sup> (i.r. and n.m.r. spectra).

**Dodecanedial (III;  $R^1 = \text{OHC}\cdot[\text{CH}_2]_{10}$ ,  $R^2 = \text{H}$ ).**—This was obtained from the corresponding benzoxathiole(II) (2.07 g, 0.005 mol) and mercury(II) chloride (8.14 g, 0.03 mol) in dimethyl sulphoxide–water (36 ml; 5 : 1 by the same procedure (reaction time 15 min; yield 98%). The aldehyde, recrystallized from methanol–water, had m.p. 65–66° (lit.,<sup>9</sup> b.p. 142–144° at 15 mmHg);  $\delta(\text{CDCl}_3)$  1.15–2.10 (m, 8 CH<sub>2</sub>), 2.30–2.65 (m, 2 CH<sub>2</sub> next to 2 CHO), and 9.93 (t, 2 CHO,  $J$  1.5 Hz).

**Reaction of 2-Phenyl-1,3-benzoxathiolylium Tetrafluoroborate (I;  $\text{Y} = \text{BF}_4$ ,  $R^1 = \text{Ph}$ ) with Methylmagnesium Iodide.**—To the Grignard reagent from methyl iodide (7.10 g, 0.05 mol) and magnesium turnings (1.17 g, 0.05 g atom) in dry ether (70–80 ml), freshly prepared or freshly recrystallized 2-phenyl-1,3-benzoxathiolylium tetrafluoroborate (3.00 g, 0.01 mol) was added at room temperature with vigorous stirring. The reaction was immediate and a brown oil separated. Stirring was continued for an additional 10 min, and then the mixture was decomposed with saturated aqueous ammonium chloride. The usual work-up produced, in almost quantitative yield, 2-methyl-2-phenyl-1,3-benzoxathiole (II;  $R^1 = \text{Ph}$ ,  $R^2 = \text{Me}$ ), identical with a previously described sample.<sup>1</sup>

**Conversion of 2-Phenyl-1,3-benzoxathiolylium Tetrafluoroborate (I;  $\text{Y} = \text{BF}_4$ ,  $R^1 = \text{Ph}$ ) into the Corresponding Perchlorate (I;  $\text{Y} = \text{ClO}_4$ ,  $R^1 = \text{Ph}$ ).**—2-Phenyl-1,3-benzoxathiolylium tetrafluoroborate (3.00 g, 0.01 mol) was dissolved in absolute ethanol (10 ml). After neutralization with sodium hydrogen carbonate, the solution was poured into water and extracted with ether. The extract was dried and evaporated to give 2-ethoxy-2-phenyl-1,3-benzoxathiole (2.37 g, 92%) (II;  $R^1 = \text{Ph}$ ,  $R^2 = \text{OEt}$ ), identical with that obtained in the same way from 2-phenyl-1,3-benzoxathiolylium perchlorate.<sup>2</sup> This was converted into the perchlorate in almost quantitative yield by the procedures previously reported.<sup>2</sup>

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<sup>7</sup> D. Greenwood and H. A. Stevenson, *J. Chem. Soc.*, 1953, 1514.

<sup>8</sup> W. F. Beech, *J. Chem. Soc.*, 1954, 1297.

<sup>9</sup> M. Meyer, *Compt. rend.*, 1937, 204, 1948.