

# Synthesis of Some Carbohydrate Cyclic Thionocarbonates Using Phase Transfer Catalysis

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Cyclic thionocarbonates are widely used as synthetic intermediates in the transformation of vicinal diols into mono-deoxygenated products<sup>1</sup> or alkenes.<sup>2</sup> Another route to the alkenes is via alkyl bis-dithiocarbonates.<sup>3</sup> Synthesis of thionocarbonates has been achieved via different routes, either by using thiocarbonyldiimidazole,<sup>4,5</sup> CS<sub>2</sub>/CH<sub>3</sub>I<sup>6,7</sup> or thiophosgene<sup>8–10</sup> with various bases. So far known, no synthesis using phase transfer catalysis has been reported.

Minor modifications of a method, using CS<sub>2</sub>, CH<sub>3</sub>I and a phase transfer catalyst, of preparing bis-dithiocarbonates,<sup>11</sup> resulted almost exclusively in the formation of cyclic thionocarbonates. An investigation of this reaction is now described.

## Results and discussion

In connection with some recent work on the synthesis of unsaturated monosaccharides we were interested in bis-dithiocarbonates. Under phase transfer conditions in a liquid–liquid (50% NaOH/CH<sub>2</sub>Cl<sub>2</sub>) two-phase system,<sup>11</sup> using CS<sub>2</sub> and CH<sub>3</sub>I as reagents, we observed that, in addition to **1c** and **2c**, the cyclic thionocarbonates **1b** and **2b** were obtained in small amounts as side products. By variation in the addition sequence (CS<sub>2</sub> was added 5 min prior to CH<sub>3</sub>I) and the molar ratios for CS<sub>2</sub> and CH<sub>3</sub>I, compounds **1b** and **2b** became the major products (2 : 1). In order to improve the ratio in favour of the cyclic thionocarbonates the reaction was investigated further. It was found that the use of a solid–liquid two-phase system, consisting of finely powdered KOH and CH<sub>2</sub>Cl<sub>2</sub> with Bu<sub>4</sub>NHSO<sub>4</sub> as the phase transfer catalyst, gave almost exclusively the thionocarbonates. The reaction was carried out at 10 °C with subsequent addition of CS<sub>2</sub> and CH<sub>3</sub>I and keeping the molar ratio of the educt, reagents and the phase-transfer catalyst approximately 1 : 1 : 1 : 1. Applying these conditions, only minor amounts (less than 5%) of by-products were obtained. A temperature of 10 °C was found to be optimal for the reaction as a lower temperature required longer reaction times, without giving higher yields, while

higher temperatures gave substantial amounts of by-products. Without, or with smaller amounts of catalyst the reaction did not work properly. All the starting materials **1a**, **2a**, **3a** and **5a** gave the cyclic thionocarbonates (Fig. 1) in high yields, and **4a** in a somewhat lower yield. The *trans* vicinal diols **6**, **7** and the 1,3-diol **8** gave no cyclic thionocarbonates. In these cases the mono-dithiocarbonates were isolated as the major products.

For the identification of **1b–5b** <sup>13</sup>C NMR spectroscopy<sup>12</sup> proved to be of great importance, taking into account that the resonance due to the thiocarbonyl carbon (OCSO) for all of the samples lay within a narrow region (189–191 ppm; Table 1). For dithiocarbonates (SCSO) a carbon resonance around 216 ppm was observed, thus allowing the clear

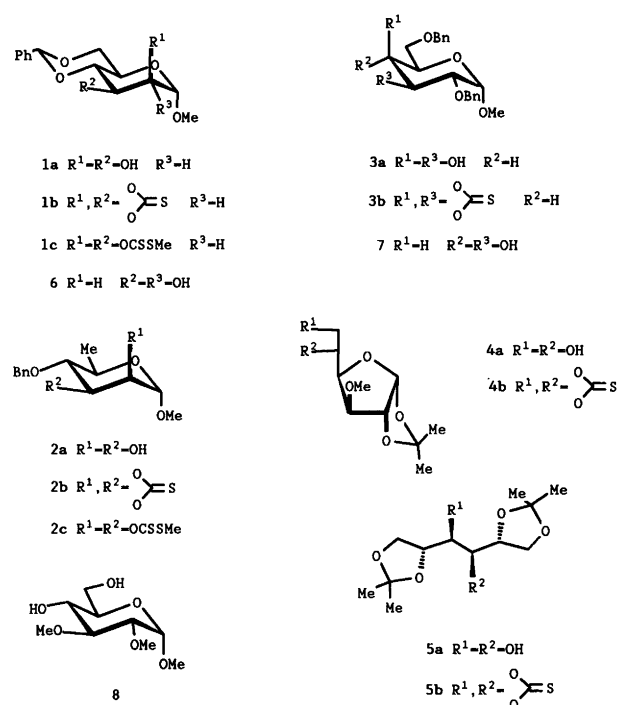


Fig. 1. Substrates and reaction products.

Table 1. Some physical data, literature data and yields for the synthesized thionocarbonates 1b–5b.

Thionocarbonate	Yield (%)	$\delta_c$ (C=S)	Physical data	Lit. data
1b	80	189.7	$[\alpha]_D -85.7^\circ$ (c 0.6) m.p. 146–147°C	m.p. 146–147°C <sup>13</sup>
2b	81	189.8	$[\alpha]_D +48.0^\circ$ (c 0.4)	
3b	73	190.6	$[\alpha]_D -6.4^\circ$ (c 1.0)	
4b	63	191.3	$[\alpha]_D -49.7^\circ$ (c 0.4) m.p. 111–112°C	$[\alpha]_D -46.5^\circ$ (c 1.0) m.p. 111–112°C <sup>14</sup>
5b	76	190.5	$[\alpha]_D -13.6^\circ$ (c 0.5) m.p. 159–161°C	m.p. 152–156°C <sup>9</sup>

classification of reaction products by means of spectroscopic data.

In the cases where either bis-dithiocarbonates or cyclic thionocarbonates can be formed this method has the advantage that, by minor variations of the reaction conditions, either product can be obtained in high yield.

### Experimental

**Typical procedure.** Methyl 4-O-benzyl-6-deoxy-2,3-O-thiocarbonyl- $\alpha$ -D-mannopyranoside (2b). The diol 2a (280 mg) and Bu<sub>4</sub>NHSO<sub>4</sub> (340 mg) were dissolved in 15 ml of CH<sub>2</sub>Cl<sub>2</sub>. The mixture was cooled to 10°C and then powdered KOH (380 mg) was added. After 5 min, CS<sub>2</sub> (83 mg) was added followed, after an additional 15 min, by CH<sub>3</sub>I (170 mg). The mixture was allowed to warm to room temperature for 15 min, and then diluted with CH<sub>2</sub>Cl<sub>2</sub> (15 ml) and washed with water (5 × 20 ml). After drying over MgSO<sub>4</sub> the solvent was removed and the remainder purified by column chromatography using hexane/CH<sub>2</sub>Cl<sub>2</sub> 3:7 as the eluant to yield 2b (253 mg, 81%) as a slightly yellow syrup,  $[\alpha]_D +48.0^\circ$  (c 0.4, CHCl<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.29 (d, 3 H, J 6.4 Hz, CH<sub>3</sub>), 3.28 (dd, 1 H, J 6.8, 9.8 Hz, H-4), 3.38 (s, 3 H, CH<sub>3</sub>O-1), 3.73 (dq, 1 H, J 6.4, 9.8 Hz, H-5), 4.73 (d, 1 H, J 7.4 Hz, H-2), 4.75 (dd, 2 H, J 11.4 Hz, CH<sub>2</sub>O-4), 4.98 (s, 1 H, H-1), 5.01 (dd, 1 H, J 6.8, 7.4 Hz, H-3), 7.35 (m, 5 H, ArH). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  17.6 (C-6), 55.1 (CH<sub>3</sub>O-1), 63.4 (C-5), 73.3 (CH<sub>2</sub>O-4), 78.7 and 80.4 (C-2 and C-3), 83.8 (C-4), 95.5 (C-1), 128.0–137.0 (Ph), 189.8 (C=S).

**NMR data for thionocarbonate 3b.** <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  3.41 (s, 3 H, CH<sub>3</sub>O-1), 3.62 (dd, 1 H, J 3.6, 7.2 Hz, H-2), 3.75 (dddd, 2 H, J 6.4, 12.8 Hz, H-6<sub>a</sub>, H-6<sub>b</sub>), 4.19

(dt, 1 H, J 2.4, 6.4 Hz, H-5), 4.59 (s, 2 H, CH<sub>2</sub>O), 4.68 (d, 1 H, J 3.6 Hz, H-1), 4.75 (dd, 2 H, CH<sub>2</sub>O), 4.91 (dd, 1 H, J 2.4, 7.2 Hz, H-4), 5.05 (t, 1 H, J 7.2 Hz, H-3), 7.35 (m, 10 H, ArH). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  55.9 (CH<sub>3</sub>O-1), 64.9 (C-5), 68.1 (C-6), 73.2, 73.7 and 74.1 (C-2 and 2 × CH<sub>2</sub>O), 79.8 and 81.3 (C-3 and C-4), 97.4 (C-1), 127.7–137.4 (Ph), 190.6 (C=S).

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