

## Synthesis of 1,3-dithiinium salts

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**Dedicated to Boris A. Trofimov on the occasion of his 65<sup>th</sup> birthday with heartiest good wishes**

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### Abstract

1,3-Dithiinium salts have been synthesized by the reactions of 1-bromo-2-acylacetylenes with dithiomalonamide or dithiomalonic acid dianilide in acetone or acetic acid or in acetic acid and an equimolar amount of perchloric acid.

**Keywords:** 1-Bromo-2-benzoylacetylene, 1-bromo-2-(2-thenoyl)acetylene, dithiomalonamide, dithiomalonic acid dianilide, 1,3-dithiins

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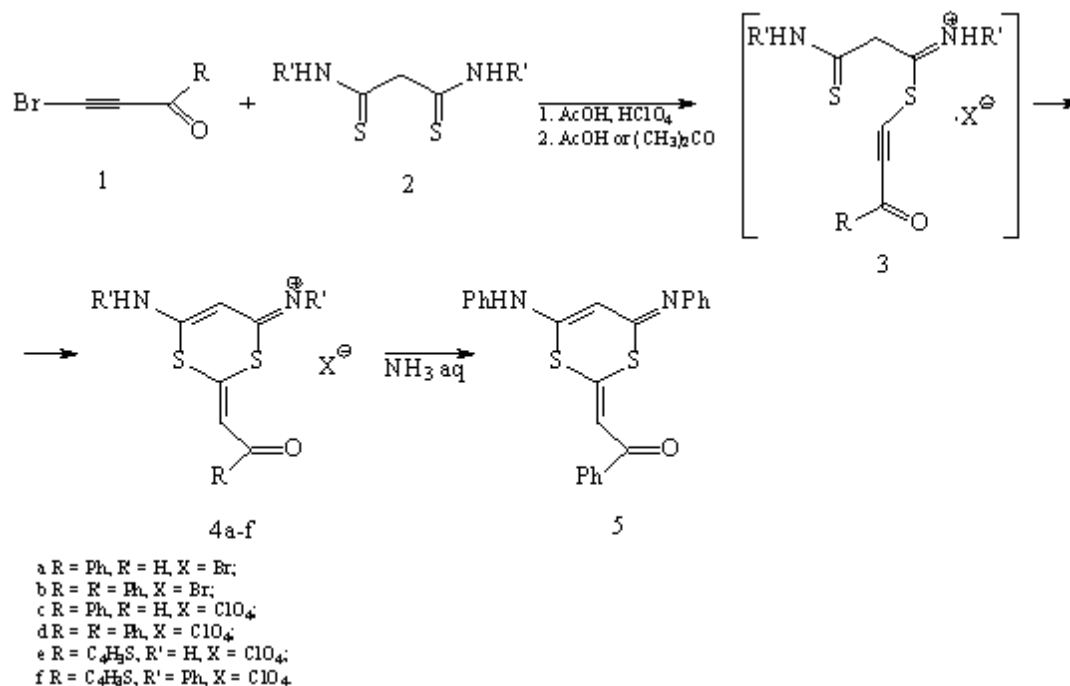
### Introduction

Generally, the reactions of N,S-containing polyfunctional nucleophiles involve sulfur and nitrogen atoms to give 1,3-thiazines<sup>1,2</sup> and 1,3-thiazolines.<sup>3,4</sup> The interaction of 1,3,5-trisubstituted-2,4-dithiobiurets and isocyanodichloride afforded an unstable 1,3,5-dithiazines which on treatment with ethanol changed into 1,3,5-triazines.<sup>5,6</sup> The data on 1,3-dithiin synthesis are meagre.<sup>7-9</sup> It has been shown that the reaction of aromatic aldehydes with hydrogen sulfide and dimethyl acetylenedicarboxylate or methyl propiolate led to 1,3-dithiins.<sup>10</sup>

### Results and Discussion

Recently we have studied the interaction of polyfunctional nucleophilic compounds with 1-bromo-2-acylacetylenes.<sup>11,12</sup> The present work deals with the reactions of dithiomalonamide or dithiomalonic acid dianilide, **2** with 1-bromo-2-benzoyl- and 1-bromo-2-(2-thenoyl)acetylenes, **1**.

It was found that the reaction in acetone or acetic acid resulted in 6-amino(2-oxo-2-phenylethylidene)-1,3-dithiin-4-iminium(phenyliminium) bromides **4a,b** instead of the expected 1,3-thiazoles.



The perchlorates of the corresponding 1,3-dithiins (**4c-f**) were isolated from the reaction mixture in acetic acid containing equimolar amounts of perchloric acid. The reaction probably took place by a cyclization involving the sulfur atom of the thiocarbonyl group followed by intermediate formation of the acyl ethynyl sulfides **3**.

The treatment of 6-anilino-2-(2-oxo-2-phenylethylidene)-1,3-dithiin-4-phenyliminium bromide **4b** with 20% aqueous ammonia solution for 7 h gave rise to the free base, 6-anilino-2-(2-oxo-2-phenylethylidene)-4-phenylimino-1,3-dithiin, **5**.

Heating of 6-anilino-2-(2-oxo-2-phenylethylidene)-1,3-dithiin-4-phenyliminium bromide **4b** in acetic acid in the presence of hydrochloric acid led to substitution of a bromide anion for the perchlorate anion.

It was impossible to obtain the free base from 6-amino-2-(2-oxo-2-phenylethylidene)-1,3-dithiin-4-iminium bromide, or to substitute a bromide ion for ClO<sub>4</sub><sup>-</sup> because of decomposition of the initial compound under these conditions. In addition, we failed to identify the decomposition products.

Apparently such behavior was caused by the presence of phenyl substituents on the nitrogen atom in compound **4b**, which stabilized the molecule and allowed the obtention of the stable 6-anilino-2-(2-oxo-2-phenylethylidene)-4-phenylimino-1,3-dithiin, **5** or the 6-anilino-2-(2-oxo-2-phenylethylidene)-1,3-dithiin-4-phenyliminium perchlorate, **4d**.

## Experimental Section

**General Procedures.** IR spectra were measured on a Specord 75 IR instrument (KBr disks).  $^1\text{H}$ - and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX 400 spectrometer (400.13 and 100.61 MHz, respectively) in  $\text{DMSO-}d_6$  with HMDS as internal standard.

**6-Amino-2-(2-oxo-2-phenylethylidene)-1,3-dithiin-4-iminium bromide (4a).** 1-Bromo-2-benzoylacetylene (0.52 g, 2.5 mmol) was slowly added to a solution of dithiomalonamide (0.34 g, 2.5 mmol) in glacial acetic acid (20 ml) under vigorous stirring at  $20^\circ$  for 7 h. The precipitate was filtered off, washed with ether, and dried in vacuum to give 0.53 g of the product (61%), m.p.  $273\text{--}275^\circ\text{C}$ . IR data,  $\nu/\text{cm}^{-1}$ , 624 (C-S), 1551–1595 (C=C, C=N), 1640 (C=O), 3059–3306 ( $\text{NH}_2$ ).  $^1\text{H}$ - NMR,  $\delta/\text{ppm}$ , 6.19 (1H, s, =CH), 9.58, 9.78 (4H, s, s,  $2\text{NH}_2$ ), 7.55–8.08 (5H, m, Ph), 8.01 (1H, s, =CHCO).  $^{13}\text{C}$ - NMR,  $\delta/\text{ppm}$ : 87.3 (CH=), 121.1 (=CHCO), 128.5, 129.0, 133.8, 136.3 (Ph), 140.2 (S-C-S), 164.6 (C- $\text{NH}_2$ ), 166.4 (C= $\text{NH}_2$ ), 186.5 (C=O). Found: C 42.27; H 3.20; Br 23.35; N 8.19; S 18.70.  $\text{C}_{12}\text{H}_{11}\text{BrN}_2\text{OS}_2$  requires C 41.99; H 3.23; Br 23.28; N 8.16; S 18.68%.

**6-Anilino-2-(2-oxo-2-phenylethylidene)-1,3-dithiin-4-phenyliminium bromide (4b).** Prepared analogously from dithiomalonic acid dianilide (0.72 g, 2.5 mmol) and 1-bromo-2-benzoylacetylene (0.52 g, 2.5 mmol). The yield of product was 0.57 g (48%). The reaction in acetone gave the product **IVb** in 27% yield, m.p.  $232\text{--}234^\circ\text{C}$ . IR data,  $\nu/\text{cm}^{-1}$  1487–1576 (C=C, C=N), 1633 (C=O).  $^1\text{H}$ - NMR,  $\delta/\text{ppm}$ : 6.34 (1H, s, =CH), 7.31–8.02 (15H, m, Ph), 7.99 (1H, s, =CHCO), 10.10 (1H, s, NH).  $^{13}\text{C}$ - NMR,  $\delta/\text{ppm}$ : 89.4 (CH=), 124.0 (=CHCO), 123.4–136.2 (Ph), 138.6 (S-C-S), 162.9 (C-N), 187.0 (C=O). Found: C 57.93; H 3.97; Br 15.86; N 6.03; S 12.93.  $\text{C}_{24}\text{H}_{19}\text{BrN}_2\text{OS}_2$  requires C 58.18; H 3.87; Br 16.18; N 5.65; S 12.94%.

**6-Amino-2-(2-oxo-2-phenylethylidene)-1,3-dithiin-4-iminium perchlorate (4c).** A solution of 1-bromo-2-benzoylacetylene (0.52 g, 2.5 mmol) and 50% aqueous  $\text{HClO}_4$  (0.29 ml, 2.5 mmol) in acetic acid (210 ml) was slowly added to a solution of dithiomalonamide (0.34 g, 2.5 mmol) in glacial acetic acid (20 ml) under vigorous stirring at  $20^\circ$  during 4 h. The precipitate was filtered, washed with ether and dried in vacuum to give the product (0.32 g, 35%), m.p.  $193\text{--}195^\circ\text{C}$ . IR data,  $\nu/\text{cm}^{-1}$  624 (C-S), 1122 ( $\text{ClO}_4^-$ ), 1543–1596 (C=C, C=N), 1624 (C=O), 3215–3305 ( $\text{NH}_2$ ).  $^1\text{H}$ - NMR,  $\delta/\text{ppm}$ : 6.10 (1H, s, =CH), 7.55–8.08 (5H, m, Ph), 8.01 (1H, s, =CHCO), 9.30, 9.35 (4H, s, s,  $2\text{NH}_2$ ).  $^{13}\text{C}$ - NMR,  $\delta/\text{ppm}$ : 88.3 (CH=), 121.9 (=CHCO), 129.3–137.0 (Ph), 140.9 (S-C-S), 165.5 (C-N), 167.4 (C= $\text{NH}_2$ ), 200.8 (C=O). Found: C 40.09; H 2.92; Cl 9.28; N 7.30; S 17.92.  $\text{C}_{12}\text{H}_{11}\text{ClN}_2\text{O}_5\text{S}_2$  requires C 39.73; H 3.06; Cl 9.77; N 7.72; S 17.68%.

**6-Anilino-2-(2-oxo-2-phenylethylidene)-1,3-dithiin-4-phenyliminium perchlorate (4d).** Prepared analogously from dithiomalonic acid dianilide (0.4 g, 1.0 mmol), 1-bromo-2-benzoylacetylene (0.2 g, 10 mmol) and 50% aqueous  $\text{HClO}_4$  (0.12 ml, 1.0 mmol). Yield 0.26 g (35%), m.p.  $223\text{--}224^\circ\text{C}$ . IR data,  $\nu/\text{cm}^{-1}$  628 (C-S), 1110 ( $\text{ClO}_4^-$ ), 1480–1600 (C=C, C=N), 1620 (C=O), 3200 (NH).  $^1\text{H}$ - NMR,  $\delta/\text{ppm}$ : 6.32 (1H, s, =CH), 7.38–8.07 (15H, m, Ph), 7.53 (1H, s,

=CHCO), 8.09 (1H, s, NH). Found: C 55.64; H 3.42; Cl 7.01; N 5.46; S 12.62. C<sub>24</sub>H<sub>19</sub>ClN<sub>2</sub>O<sub>5</sub>S<sub>2</sub> requires C 55.97; H 3.72; Cl 6.88; N 5.44; S 12.45%.

#### Substitution of Br<sup>-</sup> for ClO<sub>4</sub><sup>-</sup>

50% aqueous HClO<sub>4</sub> (0.2 g, 2 mmol) in glacial acetic acid (10 ml) was added dropwise to a solution of 6-anilino-2-(2-oxo-2-phenylethylidene)-1,3-dithiin-4-phenyliminium bromide (IVb) (0.08 g, 2.0 mmol) in glacial acetic acid (10 ml), then stirred at 20° for 4 h. The precipitate, 0.03 g (38%) was 6-anilino-2-(2-oxo-2-phenylethylidene)-1,3-dithiin-4-phenyliminium perchlorate.

**6-Amino-2-[2-oxo-2-(2-thienyl)ethylidene]-1,3-dithiin-4-iminium perchlorate (4e).** Prepared in the same way as (IVc) from dithiomalonamide (0.34 g, 2.5 mmol), 1-bromo-2-(2-thenoyl)-acetylene (0.52 g, 2.5 mmol) and 50% aqueous HClO<sub>4</sub> (0.29 ml, 2.5 mmol); yield 0.51 g (55%); m.p. 258–260°C. IR data,  $\nu/\text{cm}^{-1}$  628 (C-S), 1120 (ClO<sub>4</sub><sup>-</sup>), 1550–1594 (C=C, C=N), 1637 (C=O), 3159–3314 (NH<sub>2</sub>). <sup>1</sup>H- NMR,  $\delta/\text{ppm}$ : 6.12 (1H, s, =CH), 7.28–8.21 (3H, m, C<sub>4</sub>H<sub>3</sub>S), 7.89 (1H, s, =CHCO), 9.49, 9.60 (4H, s, s, 2NH<sub>2</sub>). <sup>13</sup>C- NMR,  $\delta/\text{ppm}$ : 87.9 (CH=), 123.1 (=CHCO), 129.04–142.54 (C<sub>4</sub>H<sub>3</sub>S), 141.0 (S-C-S), 166.1 (C=NH<sub>2</sub>), 200.0 (C=O). Found: C 32.12; H 2.88; Cl 9.26; N 7.88; S 26.46. C<sub>10</sub>H<sub>9</sub>ClN<sub>2</sub>O<sub>5</sub>S<sub>3</sub> requires C 32.56; H 2.46; Cl 9.61; N 7.59; S 26.08%.

**6-Anilino-2-[2-oxo-2-(2-thienyl)ethylidene]-1,3-dithiin-4-phenyliminium perchlorate (4f).** Prepared analogously from dithiomalonic acid dianilide (0.22 g, 1.0 mmol), 1-bromo-2-(2-thenoyl)-acetylene (0.22 g, 1.0 mmol) and 50% aqueous HClO<sub>4</sub> (0.12 ml, 1.0 mmol). The yield was 0.3 g (43%); m.p. 221–223°C. IR data,  $\nu/\text{cm}^{-1}$ : 628 (C-S), 1110 (ClO<sub>4</sub><sup>-</sup>), 1500–1580 (C=C, C=N), 1620 (C=O). <sup>1</sup>H- NMR,  $\delta/\text{ppm}$ : 6.20 (1H, s, =CH), 7.21–8.25 (3H, m, C<sub>4</sub>H<sub>3</sub>S), 7.92 (1H, s, =CHCO), 9.58 (1H, s, NH). <sup>13</sup>C- NMR,  $\delta/\text{ppm}$ : 88.1 (CH=), 122.8 (=CHCO), 129.1–142.58 (C<sub>4</sub>H<sub>3</sub>S), 141.25 (S-C-S), 166.3 (C=NH), 200.0 (C=O). Found: C 50.62; H 3.29; Cl 7.12; N 5.30; S 18.23. C<sub>22</sub>H<sub>17</sub>ClN<sub>2</sub>O<sub>5</sub>S<sub>3</sub> requires: C 50.71; H 3.29; Cl 6.80; N 5.29; S 18.46%.

**6-Anilino-2-(2-oxo-2-phenylethylidene)-4-phenylimino-1,3-dithiin (5).** 6-Anilino-2-(2-oxo-2-phenylethylidene)-1,3-dithiin-4-phenyliminium bromide (IVb) (0.3 g, 6.0 mmol) was stirred in 20% aqueous ammonia for 8 h. The precipitate was filtered, washed with water and dried in vacuum; yield 0.21 g (84%); m.p. 96–98°C. IR data,  $\nu/\text{cm}^{-1}$ : 1487–1600 (C=C, C=N), 1625 (C=O). <sup>1</sup>H- NMR,  $\delta/\text{ppm}$ : 6.38 (1H, s, =CH), 7.35–8.04 (15H, m, Ph), 8.01 (1H, s, =CHCO), 10.02 (1H, s, NH). <sup>13</sup>C NMR,  $\delta/\text{ppm}$ : 89.0 (CH=), 124.3 (=CHCO), 123.03–136.4 (Ph), 138.2 (S-C-S), 163.03 (C-N), 188.03 (C=O). Found: C 53.93; H 3.61; N 22.74; S 12.93. C<sub>24</sub>H<sub>18</sub>N<sub>2</sub>O<sub>5</sub>S<sub>2</sub> requires: C 53.86; H 3.70; N 22.84; S 13.07%.

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