Article

Indium-Catalyzed Direct Conversion of Lactones into Thiolactones Using a Disilathiane as a Sulfur Source

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Abstract: Indium-catalyzed reaction of lactones and a disilathiane leading to thiolactones is described. The direct synthesis of thiolactones from lactones with an appropriate sulfur source is one of the most attractive approaches in organic and pharmaceutical chemistry. In this context, we found an indium-catalyzed direct conversion of lactones into thiolactones in the presence of elemental sulfur and a hydrosilane via formation of the disilathiane in-situ. On the basis of the previous reaction, the application utilizing the disilathiane as a sulfur source was performed herein for the efficient synthesis of a variety of thiolactone derivatives from lactones by an indium-catalyst.

Keywords: indium-catalyst; disilathiane; lactones; thiolactones.

1. Introduction

The introduction of sulfur atom to organic molecules is a significant topic in synthetic chemistry because it potentially provides the complex and important sulfur-containing compounds directly. Therefore, a search for undiscovered sulfur source that could be applicable to organic sulfur chemistry is imperative, and extensive efforts have been devoted for development of molecular transformations utilizing a novel sulfur source by many research groups thus far [1–6]. In this context, our group have demonstrated that the copper-catalyzed construction of diaryl sulfides from aryl iodides and hexamethyldisilathiane, (Me2Si)2S [7]. In the reaction, the disilathiane functioned as a novel and effective S1 source of sulfides, and the results encouraged us that the strategy employing the disilathiane could be acceptable for any other sulfur-introduction reactions [8–12].

Recently, we also reported the indium-catalyzed reductive conversion of lactones 1 into thiolactones 2 using a combination of elemental sulfur (S) and a hydrosilane, wherein the generation of a disilathiane ([Si]2S) from S and a hydrosilane is a key process for the formation of thiolactones 2 (Scheme 1a) [13]. Although the in-situ formation strategy of the disilathiane is useful and easily-handling procedure, the yields of thiolactones 2 obtained by the method remained in low to moderate levels. We envisioned that the problem could be overcome by utilizing the activated disilathiane, which can be easily prepared from S and a hydrosilane in advance. Herein, we describe the indium-catalyzed direct formation of thiolactones 2 from lactones 1 using hexamethyldisilathiane as an effective S1 source (Scheme 1b).
2. Results and Discussion

On the bases of our previous study on the InCl₃-catalyzed transformation of lactones 1 to thiolactones 2 employing elemental sulfur (S₈) and a hydrosilane, the optimization studies utilizing a disilathiane as a sulfur source were initially conducted (Table 1). When γ-phenyl-γ-butyrolactone (1a) was treated with 1.1 equiv of hexamethyldisilathiane, (Me₃Si)₂S, in the presence of 5 mol % of InCl₃ in 1,2-dichlorobenzene at 80 °C for 24 h, the corresponding γ-butyrothiolactone 2a was obtained in a 77% GC yield (entry 1). The formation of 2a was also observed in the cases with other indium(III) catalysts, such as InBr₃, InI₃, In(OAc)₃, and In(OTf)₃, in good yields (entries 2–5). Especially, In(OTf)₃ proved to be the most effective catalyst for the reaction, shown in entry 5, which provided 2a in a 99% GC yield with a 94% isolated yield. In contrast, in the absence of the catalyst, the thiolactone was not generated (entry 6). Although several solvents (chlorobenzene, 1,2-dichloroethane, and toluene) were acceptable to the reaction, these yields were not higher than that using 1,2-Cl₂C₆H₄ as a solvent (entries 7–9 vs entry 5). The reaction with lower catalyst loading (1 mol % of In(OTf)₃) was also possible to form 2a in a 97% GC yield, then the product was isolated in an 83% yield (entry 10). Employing a stoichiometric amount of TfOH instead of In(OTf)₃ catalyst provided the thiolactone quantitatively (entry 11), whereas its application to the TfOH-catalyzed reaction did not proceed well (entry 12).

Table 1. Screening of the reaction conditions for the catalytic conversion of 1a to 2a.a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>GC yield of 2a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>InCl₃ (5 mol %)</td>
<td>1,2-Cl₂C₆H₄</td>
<td>77</td>
</tr>
<tr>
<td>2</td>
<td>InBr₃ (5 mol %)</td>
<td>1,2-Cl₂C₆H₄</td>
<td>62</td>
</tr>
<tr>
<td>3</td>
<td>InI₃ (5 mol %)</td>
<td>1,2-Cl₂C₆H₄</td>
<td>69</td>
</tr>
<tr>
<td>4</td>
<td>In(OAc)₃ (5 mol %)</td>
<td>1,2-Cl₂C₆H₄</td>
<td>78</td>
</tr>
<tr>
<td>5</td>
<td>In(OTf)₃ (5 mol %)</td>
<td>1,2-Cl₂C₆H₄</td>
<td>99 (94)¹</td>
</tr>
<tr>
<td>6</td>
<td>none</td>
<td>1,2-Cl₂C₆H₄</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>In(OTf)₃ (5 mol %)</td>
<td>ClC₆H₅</td>
<td>76</td>
</tr>
</tbody>
</table>

a) Previous work

Scheme 1. Indium-catalyzed conversion of lactones 1 to thiolactones 2.
<table>
<thead>
<tr>
<th>Entry</th>
<th>Lactone 1</th>
<th>Thiolactone 2</th>
<th>Isolated yield of ( \text{thiolactone} ) 2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Conditions A</td>
</tr>
<tr>
<td>1</td>
<td>1b (R = 2-Me)</td>
<td>2b</td>
<td>73</td>
</tr>
<tr>
<td>2</td>
<td>1c (R = 3-Me)</td>
<td>2c</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>1d (R = 4-Me)</td>
<td>2d</td>
<td>64</td>
</tr>
<tr>
<td>4</td>
<td>1e (R = 2,5-Me)</td>
<td>2e</td>
<td>65</td>
</tr>
<tr>
<td>5</td>
<td>1f (R = 4-Ph)</td>
<td>2f</td>
<td>61</td>
</tr>
<tr>
<td>6</td>
<td>1g (R = 3-MeO)</td>
<td>2g</td>
<td>79</td>
</tr>
<tr>
<td>7</td>
<td>1h (R = 4-MeO)</td>
<td>2h</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>1i (R = 4-F)</td>
<td>2i</td>
<td>79</td>
</tr>
<tr>
<td>9</td>
<td>1j (R = 4-Cl)</td>
<td>2j</td>
<td>87</td>
</tr>
<tr>
<td>10</td>
<td>1k (R = 4-Br)</td>
<td>2k</td>
<td>74</td>
</tr>
</tbody>
</table>
Finally, the present procedure was evaluated using substrates involving an ester moiety, but not lactones. When phthalic anhydride (1u) was treated with a disilathiane, the corresponding reaction proceeded to give thiophthalic anhydride (2u) in a 74% isolated yield (eq 1).

![Chemical structures and reaction equation]

\[ 1u + (\text{Me}_3\text{Si})_2\text{S} \xrightarrow{\text{1.1 equiv}} \text{ln(OTf)}_3 (1 \text{ mol %}) \xrightarrow{1,2-\text{Cl}_2\text{C}_6\text{H}_4 \text{OTf}} 2\text{u}, 74\% \]
Although an acyclic ester, methyl benzoate derivative 1v, was not acceptable to the transformation under the optimal conditions, the use of 5 mol % of InI₃ catalyst at 120 °C for 20 h improve the reactivity for the reaction, leading to the expected thioester 2v in a 38% isolated yield. Along with the formation of thioester 2v in that conditions, the unexpected dithioester 3v was also isolated in an 18% yield (Scheme 2).

![Chemical structure of 1v, 2v, and 3v](image)

**Scheme 2.** Reaction of an acyclic ester.

### 3. Materials and Methods

#### 3.1. General Information

¹H and ¹³C NMR spectra were recorded on a 300 or 500 MHz spectrometer. Chemical shifts in the ¹H and ¹³C NMR spectra were reported in ppm relative to the residual solvent peaks such as those of chloroform (δ 7.26 for ¹H, and δ 77.0 for ¹³C) or of the internal reference tetramethylsilane (δ 0.00 for both ¹H and ¹³C). High-resolution mass spectra (HRMS) were measured using NBA (3-nitrobenzylalcohol) as a matrix. GC analyses were performed using a DB-5 capillary column (30 m × 0.25 mm, film thickness = 0.25 μm). Reactions were monitored by TLC analysis of the reaction aliquots. Column chromatography was performed using a silica gel. All indium compounds and hexamethyldisilathiane were commercially available and were used without further purification. 1,2-Dichlorobenzene was distilled from CaH₂. Lactones 1a, 1f, 1n, 1o, 1q, and phthalic anhydride (1u), and an ester 1v were purchased and used without further purification. Lactones 1b and 1l were prepared by the gallium-catalyzed reductive cyclization of keto acids [14]. Lactones 1c, 1d, 1e, 1g, 1h, 1i, 1j, 1k, 1m, 1p, and 1r, and 1s were prepared via modified literature method [15].

#### 3.2. General Procedure A for the Indium-Catalyzed Conversion of Lactones or Its Derivatives 1 into Thiolactones 2 Using a Disilathiane (In the case of 1 in solid state at room temperature)

To a screw-capped tube, lactone or the derivative 1 (0.50 mmol) was added. The tube was sealed and moved into a glovebox, then In(OTf)₃ (2.8 mg, 0.0050 mmol) was added. The tube was sealed again and removed from the glovebox. 1,2-Dichlorobenzene (0.5 mL) and hexamethyldisilathiane (98.1 mg, 0.550 mmol) were successively added, and after the tube was sealed, the mixture was heated at 80 °C for 24 h. The resulting mixture was cooled to room temperature, and chloroform was added. The mixture was transferred into a round-bottom flask, which was then evaporated under the reduced pressure. The crude material was purified by a silica gel column chromatography (hexane/EtOAc), followed by a gel permeation chromatography (GPC) in some cases.

#### 3.3. General Procedure B for the Indium-Catalyzed Conversion of Lactones 1 into Thiolactones 2 Using a Disilathiane (In the case of 1 in liquid state at room temperature)
To a screw-capped tube, In(OTf)₃ (2.8 mg, 0.0050 mmol) was added in a glovebox. The tube was then sealed and removed from the glovebox, 1,2-dichlorobenzene (0.5 mL), lactone 1 (0.50 mmol), and hexamethyldisilathiane (98.1 mg, 0.550 mmol) were added in this order. After the tube was sealed, the mixture was heated at 80 °C for 24 h. The resulting mixture was cooled to room temperature, and chloroform was added. The mixture was transferred into a round-bottom flask, which was then evaporated under the reduced pressure. The crude material was purified by a silica gel column chromatography (hexane/EtOAc), followed by a gel permeation chromatography (GPC) in some cases.

### 3.4. Product Characterization

**Dihydro-5-phenyl-(2H)-thiophene (2a)** [13]. General procedure A was followed with 5-phenylidihydropyran-2-one (1a, 80.2 mg). Column chromatography (10/1 hexane/EtOAc) afforded 2a as a colorless oil (73.4 mg, 83%): ¹H NMR (CDCl₃, 500 MHz) δ 2.22–2.30 (m, 1 H, CH₃), 2.57–2.79 (m, 3 H, CH₂, CH₃), 4.99 (dd, J = 10.0, 5.5 Hz, 1 H, ArH); ¹³C NMR (CDCl₃, 125 MHz) δ 34.9, 42.8, 54.2, 127.3, 128.7, 128.8, 139.4, 207.8; MS (EI) m/z (%) 178 (M⁺, 78), 117 (100).

**Dihydro-5-(2-methylphenyl)-(2H)-thiophene (2b)** [13]. General procedure B was followed with 5-(2-methylphenyl)dihydropyran-2-one (1b, 89.9 mg). Column chromatography (10/1 hexane/EtOAc) afforded 2b as a colorless oil (69.7 mg, 73%): ¹H NMR (CDCl₃, 500 MHz) δ 2.26–2.34 (m, 1 H, CH₂), 2.42 (s, 3 H, CH₃), 2.55–2.60 (m, 1 H, CH₂), 2.67–2.74 (m, 1 H, CH₂), 2.77–2.83 (m, 1 H, CH₂), 5.25 (dd, J = 9.5, 5.5 Hz, 1 H, CH), 7.20–7.21 (m, 3 H, ArH), 7.55 (d, J = 8.0 Hz, 1 H, ArH); ¹³C NMR (CDCl₃, 125 MHz) δ 19.5, 33.4, 42.7, 50.3, 126.5, 126.7, 127.8, 130.7, 135.7, 137.2, 208.0; MS (EI) m/z (%) 192 (M⁺, 82), 117 (100).

**Dihydro-5-(3-methylphenyl)-(2H)-thiophene (2c)** [13]. General procedure B was followed with 5-(3-methylphenyl)dihydropyran-2-one (1c, 92.3 mg). Column chromatography (10/1 hexane/EtOAc) afforded 2c as a yellow oil (81.9 mg, 82%): ¹H NMR (CDCl₃, 500 MHz) δ 2.25–2.29 (m, 1 H, CH₂), 2.37 (s, 3 H, CH₃), 2.58–2.80 (m, 3 H, CH₂, CH₃), 4.96 (dd, J = 10.0, 5.5 Hz, 1 H, CH), 7.13 (d, J = 7.0 Hz, 1 H, ArH), 7.21–7.27 (m, 3 H, ArH); ¹³C NMR (CDCl₃, 125 MHz) δ 21.4, 35.0, 42.9, 54.3, 124.4, 128.1, 128.7, 128.9, 139.3, 208.0; MS (EI) m/z (%) 192 (M⁺, 100).

**Dihydro-5-(4-methylphenyl)-(2H)-thiophene (2d)** [13]. General procedure A was followed with 5-(4-methylphenyl)dihydropyran-2-one (1d, 87.5 mg). Column chromatography (10/1 hexane/EtOAc) afforded 2d as a colorless oil (61.3 mg, 64%): ¹H NMR (CDCl₃, 500 MHz) δ 2.21–2.29 (m, 1 H, CH₂), 2.35 (s, 3 H, CH₃), 2.56–2.78 (m, 3 H, CH₂, CH₃), 4.96 (dd, J = 10.0, 5.5 Hz, 1 H, CH), 7.17 (d, J = 8.0 Hz, 2 H, ArH), 7.30 (d, J = 8.0 Hz, 2 H, ArH); ¹³C NMR (CDCl₃, 125 MHz) δ 21.0, 35.0, 42.9, 54.1, 127.2, 129.5, 136.4, 137.9, 208.0; MS (EI) m/z (%) 192 (M⁺, 82), 117 (100).

**Dihydro-5-(2,5-dimethylphenyl)-(2H)-thiophene (2e)** [13]. General procedure A was followed with 5-(2,5-dimethylphenyl)dihydropyran-2-one (1e, 94.5 mg). Column chromatography (10/1 hexane/EtOAc) afforded 2e as a yellow oil (66.6 mg, 65%): ¹H NMR (CDCl₃, 500 MHz) δ 2.24–2.31 (m, 1 H, CH₂), 2.33 (s, 3 H, CH₃), 2.36 (s, 3 H, CH₃), 2.53–2.58 (m, 1 H, CH₂), 2.65–2.73 (m, 1 H, CH₂), 2.76–2.82 (m, 1 H, CH₂), 5.22 (dd, J = 10.0, 5.5 Hz, 1 H, CH), 7.01 (d, J = 7.5 Hz, 1 H, ArH), 7.07 (d, J = 7.5 Hz, 1 H, ArH), 7.36 (s, 1 H, ArH); ¹³C NMR (CDCl₃, 125 MHz) δ 19.0, 21.0, 33.4, 42.7, 50.3, 127.1, 128.5, 130.6, 132.5, 136.2, 136.9, 208.1; MS (EI) m/z (%) 206 (M⁺, 85), 131 (100).

**Dihydro-5-(1,1′-biphenyl)-4-yl-(2H)-thiophene (2f)**. General procedure A was followed with 5-(1,1′-Biphenyl)-4-ylidihydropyran-2-one (1f, 96.2 mg). Column chromatography (10/1 hexane/EtOAc) and GPC afforded 2f as a colorless solid (61.6 mg, 61%); mp 120–121 °C; ¹H NMR (CDCl₃, 500 MHz) δ 2.78–2.36 (m, 1 H, CH₂), 2.63–2.83 (m, 3 H, CH₂, CH₃), 5.05 (dd, J = 10.0, 5.5 Hz, 1 H, CH), 7.35–7.61 (m, 9 H, ArH); ¹³C NMR (CDCl₃, 125 MHz) δ 35.0, 42.9, 54.1, 127.0, 127.5, 127.6, 127.9, 128.8, 138.4, 140.4, 141.1, 207.8; MS (EI) m/z (%) 254 (M⁺, 100); HRMS (EI) calc for [M⁺]
(C₂₆H₂₃OS) m/z 254.0765, found 254.0771.
Column chromatography afforded 2g as a colorless solid (23.2 mg, 22%): \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 7.12 (m, 2 H, ArH); \(^1^3\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 35.4, 42.7, 53.5, 128.7, 129.0, 133.8, 138.0, 207.2; MS (EI) \(m/z\) (%) 232 (M\(^+\), 29), 212 (M\(^+\), 83), 117 (100).

### Dihydro-5-(5,6,7,8-tetrahydronapthalen-2-yl)-(3H)-thiophenone (2l) [13]

General procedure B was followed with 5-(5,6,7,8-Tetrahydronapthalen-2-yl)dihydrofuran-2-one (1l, 96.3 mg). Column chromatography (10/1 hexane/EtOAc) afforded 2l as a colorless oil (86.3 mg, 79%): \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 7.38–7.42 (m, 4 H, ArH); \(^1^3\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 34.9, 42.7, 53.5, 128.7, 129.0, 133.8, 138.0, 207.2; MS (EI) \(m/z\) (%) 232 (M\(^+\), 29), 212 (M\(^+\), 83), 117 (100).

### Dihydro-5-(5,6,7,8-tetrahydronapthalen-2-yl)-(3H)-thiophenone (2m) [13]

General procedure B was followed with 5-(5,6,7,8-Tetrahydronapthalen-2-yl)dihydrofuran-2-one (1m, 89.0 mg). Column chromatography (10/1 hexane/EtOAc) afforded 2m as a colorless oil (22.3 mg, 33%): \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 7.38–7.42 (m, 4 H, ArH); \(^1^3\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 34.9, 42.7, 53.5, 128.7, 129.0, 133.8, 138.0, 207.2; MS (EI) \(m/z\) (%) 232 (M\(^+\), 100).
Thiophthalide (2o) [16]. General procedure A was followed with phthalide (1o, 67.6 mg). Column chromatography (10/1 hexane/EtOAc) afforded 2o as a colorless solid (26.8 mg, 18%): mp 68–70 °C; 1H NMR (CDCl₃, 500 MHz) δ 4.48 (s, 2 H, CH₂), 7.48 (dd, J = 7.5, 7.5 Hz, 1 H, ArH), 7.55 (d, J = 7.0 Hz, 1 H, ArH), 7.63 (dd, J = 7.5, 7.5 Hz, 1 H, ArH), 7.85 (d, J = 7.5 Hz, 1 H, ArH); ¹³C NMR (CDCl₃, 125 MHz) δ 34.6, 123.9, 126.3, 128.0, 133.1, 135.8, 147.0, 198.0; MS (EI) m/z (%) 150 (M⁺, 89), 121 (100).

3-Phenyl-benzo[b][thiophen-1(3H)-one] (2p) [13]. General procedure A was followed with 3-phenylisobenzofuran-1-one (1p, 105.9 mg). Column chromatography (10/1 hexane/EtOAc) afforded 2p as a pale yellow solid (7.5 mg, 85%): mp 87–88 °C; ¹H NMR (CDCl₃, 500 MHz) δ 5.91 (s, 1 H, CH), 7.25–7.36 (m, 6 H, ArH), 7.48 (dd, J = 7.5, 7.5 Hz, 1 H, ArH), 7.56 (dd, J = 7.5, 7.5 Hz, 1 H, ArH), 7.86 (d, J = 7.5 Hz, 1 H, ArH); ¹³C NMR (CDCl₃, 125 MHz) δ 54.6, 123.6, 126.6, 128.29, 128.33, 128.4, 129.1, 133.6, 135.7, 138.8, 151.2, 197.2; MS (EI) m/z (%) 226 (M⁺, 100).

Tetrahydro-6-phenyl-2H-benzo[b]thiophen-2-one (2q) [13]. General procedure A was followed with tetrahydro-6-phenyl-2H-pyran-2-one (1q, 89.3 mg). Column chromatography (10/1 hexane/EtOAc) afforded 2q as an orange oil (9.7 mg, 10%); ¹H NMR (CDCl₃, 500 MHz) δ 1.94–2.10 (m, 2 H, CH₂), 2.14–2.19 (m, 1 H, CH₂), 2.37–2.41 (m, 1 H, CH₂), 2.57–2.43 (m, 1 H, CH₂), 2.59–2.78 (m, 1 H, CH₃), 4.65 (dd, J = 11.0, 4.0 Hz, 1 H, CH), 7.29–7.32 (m, 1 H, ArH), 7.35–7.39 (m, 4 H, ArH); ¹³C NMR (CDCl₃, 125 MHz) δ 22.7, 32.4, 40.5, 50.5, 127.7, 128.1, 128.9, 140.4, 201.3; MS (EI) m/z (%) 192 (M⁺, 59), 104 (100).

Tetrahydro-6-(4-methylphenyl)-2H-thiophen-2-one (2r). General procedure A was followed with tetrahydro-6-(4-methylphenyl)-2H-pyran-2-one (1r, 92.3 mg). Column chromatography (10/1 hexane/EtOAc) and GPC afforded 2r as a colorless oil (9.5 mg, 9%); ¹H NMR (CDCl₃, 500 MHz) δ 1.93–2.07 (m, 2 H, CH₂), 2.15–2.17 (m, 1 H, CH₂), 2.35 (s, 3 H, CH₃), 2.37–2.44 (m, 1 H, CH₂), 2.72–2.76 (m, 1 H, CH₂), 4.61 (dd, J = 11.0, 3.5 Hz, 1 H, CH), 7.17 (d, J = 7.5 Hz, 2 H, ArH), 7.26 (d, J = 7.5 Hz, 2 H, ArH); ¹³C NMR (CDCl₃, 125 MHz) δ 21.1, 22.7, 32.4, 40.5, 50.2, 127.5, 129.5, 137.4, 137.9, 201.6; MS (EI) m/z (%) 206 (M⁺, 62), 118 (100); HRMS (ESI) calcld for [M⁺]⁺ (C₁₆H₁₂OS) m/z 206.0765, found 206.0766.

6-(4-Chlorophenyl)tetrahydro-2H-thiophen-2-one (2s). General procedure A was followed with 6-(4-chlorophenyl)tetrahydro-2H-pyran-2-one (1s, 107.5 mg). Column chromatography (10/1 hexane/EtOAc) and GPC afforded 2s as a colorless oil (4.8 mg, 4%); ¹H NMR (CDCl₃, 500 MHz) δ 1.93–2.02 (m, 2 H, CH₂), 2.04–2.19 (m, 1 H, CH₂), 2.34–2.39 (m, 1 H, CH₂), 2.56–2.63 (m, 1 H, CH₃), 2.73–2.78 (m, 1 H, CH₂), 4.62 (dd, J = 11.0, 4.5 Hz, 1 H, CH), 7.30–7.35 (m, 4 H, ArH); ¹³C NMR (CDCl₃, 125 MHz) δ 22.6, 32.4, 40.5, 49.7, 129.0, 129.1, 133.9, 139.0, 200.8; MS (EI) m/z (%) 226 (M⁺+2, 20), 210 (M⁺, 23), 138 (100); HRMS (ESI) calcld for [M⁺]⁺ (C₁₃H₁₀ClOS) m/z 226.0219, found 226.0241.

1,4-Dihydro-3H-2-benzothioypyrain-3-one (2t) [13]. General procedure A was followed with 1,4-dihydro-3H-2-benzyopyran-3-one (1t, 74.3 mg). Column chromatography (10/1 hexane/EtOAc) afforded 2t as a pale yellow solid (40.9 mg, 50%): mp 90–93 °C; ¹H NMR (CDCl₃, 500 MHz) δ 3.79 (s, 2 H, CH₂), 4.22 (s, 2 H, CH₂), 7.21–7.32 (m, 4 H, ArH); ¹³C NMR (CDCl₃, 125 MHz) δ 34.2, 49.2, 126.6, 127.4, 128.0, 128.7, 133.7, 134.2, 202.9; MS (EI) m/z (%) 164 (M⁺, 14), 104 (100).

Phthalic thioanhydride (2u) [17]. General procedure A was followed with phthalic anhydride (1u, 77.3 mg). Column chromatography (10/1 hexane/EtOAc) afforded 2u as a yellow solid (56.1 mg, 74%): mp 68–70 °C; ¹H NMR (CDCl₃, 500 MHz) δ 7.81–7.83 (m, 2 H, ArH), 7.97–7.99 (m, 2 H, ArH); ¹³C NMR (CDCl₃, 125 MHz) δ 123.8, 135.0, 138.7, 189.8; MS (EI) m/z (%) 164 (M⁺, 100).

S-Methyl 4-methylbenzothioate (2v). General procedure A was followed with methyl 4-methylbenzoate (1v, 75.0 mg). Column chromatography (100/1 hexane/EtOAc) afforded 2v as a red oil (31.8 mg, 38%): ¹H NMR (CDCl₃, 500 MHz) δ 2.40 (s, 3 H, CH₃), 2.46 (s, 3 H, CH₃), 7.24 (d, J = 14.5
Methyl 4-methylbenzodithioate (3v) [18]. General procedure A was followed with methyl 4-methylbenzoate (1v, 75.0 mg). Column chromatography (100/1 hexane/EtOAc) afforded 3v as an orange oil (15.9 mg, 18%): 1H NMR (CDCl₃, 500 MHz) δ 2.38 (s, 3 H, CH₃), 2.77 (s, 3 H, CH₃), 7.18 (d, J = 13.5 Hz, 2 H, ArH); 13C NMR (CDCl₃, 125 MHz) δ 13.5, 144.1, 192.1; MS (EI) m/z (%): 166 (M⁺, 5), 119 (100).

5-[1,1'-Biphenyl]-4-yldihydro-2H-furanone (1f). A colorless solid: mp 100–102 °C; 1H NMR (CDCl₃, 500 MHz) δ 2.19–2.29 (m, 1 H, CH₂), 2.66–2.72 (m, 3 H, CH₃), 5.54–5.57 (m, 1 H, CH), 7.35–7.46 (m, 5 H, ArH), 7.58–7.62 (m, 4 H, ArH); 13C NMR (CDCl₃, 125 MHz) δ 29.0, 30.9, 81.0, 125.8, 127.1, 127.45, 127.53, 128.8, 138.3, 140.4, 141.4, 176.9; MS (EI) m/z (%): 182 (M⁺, 100); HRMS (EI) calcd for [M⁺] (C₁₀H₉O) m/z 238.0994, found 238.1002.

Tetrahydro-6-(4-methylphenyl)-2H-pyran-2-one (1r). A colorless solid: mp 81–83 °C; 1H NMR (CDCl₃, 500 MHz) δ 1.80–1.88 (m, 1 H, CH₂), 1.92–1.98 (m, 2 H, CH₂), 2.09–2.14 (m, 1 H, CH₂), 2.34 (s, 3 H, CH₃), 2.51–2.56 (m, 1 H, CH₂), 2.57–2.71 (m, 1 H, CH₂), 5.30 (dd, J = 10.5, 3.5 Hz, 1 H, CH), 7.17 (d, J = 7.5 Hz, 2 H, ArH), 7.22 (d, J = 7.5 Hz, 2 H, ArH); 13C NMR (CDCl₃, 125 MHz) δ 18.4, 21.0, 29.3, 30.3, 81.5, 125.9, 136.1, 136.8, 171.1; MS (EI) m/z (%): 190 (M⁺, 42), 118 (100); HRMS (EI) calcd for [M⁺] (C₁₅H₁₃O) m/z 238.0994, found 238.1095.

Tetrahydro-6-(4-chlorophenyl)-2H-pyran-2-one (1s). An orange solid: mp 91–98 °C; 1H NMR (CDCl₃, 500 MHz) δ 1.77–1.85 (m, 1 H, CH₂), 1.96–2.01 (m, 2 H, CH₂), 2.12–2.16 (m, 1 H, CH₂), 2.53–2.60 (m, 1 H, CH₂), 2.67–2.73 (m, 1 H, CH₂), 5.32 (dd, J = 10.5, 3.0 Hz, 1 H, CH), 7.28 (d, J = 8.5 Hz, 2 H, ArH), 7.34 (d, J = 8.5 Hz, 2 H, ArH); 13C NMR (CDCl₃, 125 MHz) δ 18.4, 29.3, 30.4, 80.8, 127.0, 128.6, 133.9, 138.2, 171.1; MS (EI) m/z (%): 212 (M⁺, 7), 210 (M⁺, 23), 70 (100); HRMS (EI) calcd for [M⁺] (C₁₅H₁₁ClO) m/z 210.0448, found 210.0449.

4. Conclusions

An indium-catalyzed formation of thiolactones from lactones and a disilathiane was developed. A disilathiane was found to be a novel and an effective sulfur source for this type of conversion, and a wide range of lactone derivatives were successfully converted into the corresponding thiolactones.

Supplementary Materials: The following are available online at www.mdpi.com/... 1H and 13C NMR spectra.

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References


**Sample Availability:** Samples of the compounds are not available from the authors.