

## 2,5-Bis-(butylsulfanyl)-2,3-dihydro-4H-pyran-2-carbaldehyde in the synthesis of five-membered heterocycles

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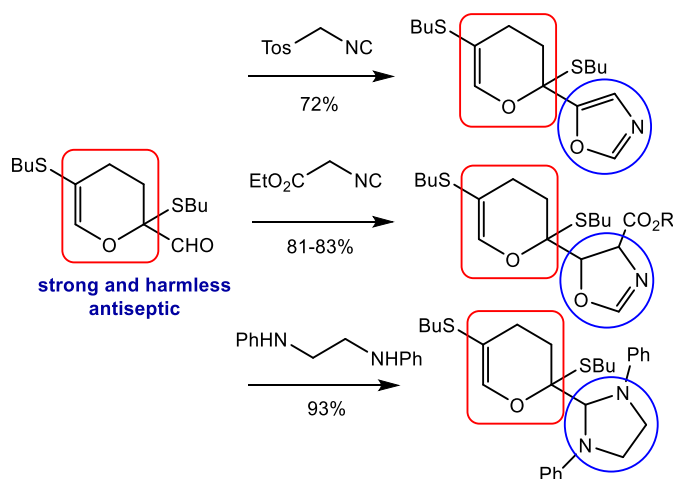
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### Abstract

Five-membered, nitrogen-containing heterocycles such as oxazole, oxazoline and imidazolidine are important structural motifs of many natural and synthetic compounds, as well as drugs with diverse bioactivity. An efficient strategy for the synthesis of new heterocyclic compounds such as 1,3-oxazole, 1,3-oxazoline and 1,3-imidazolidine from 2,5-bis-(butylsulfanyl)-2,3-dihydro-4H-pyran-2-carbaldehyde has been developed.



**Keywords:** Dihydropyran, heterocycles, 1,3-oxazole, 1,3-oxazoline, 1,3-imidazolidine

## Introduction

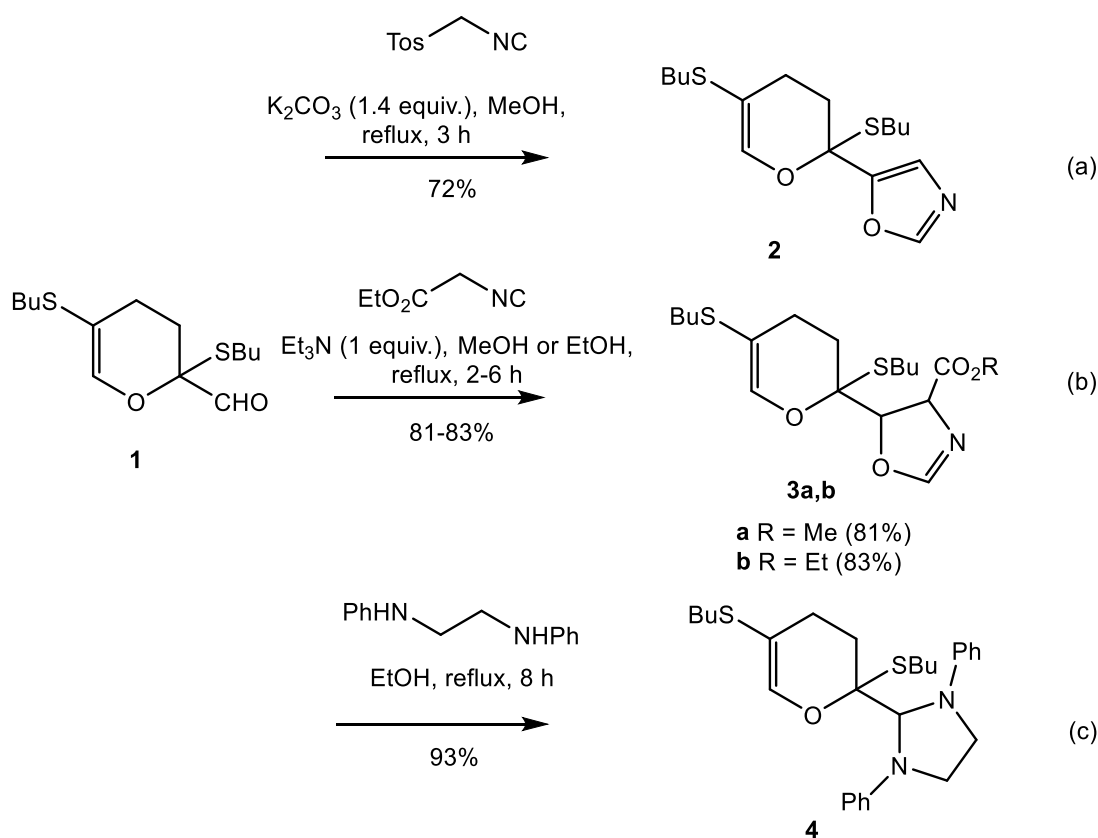
The dihydropyran structural motif is found in a range of natural products, and is of interest in pharmaceutical-chemistry applications.<sup>1-5</sup> For example, a commercial antiviral drug, Zanamivir, contains the dihydropyran core.<sup>6</sup> A great deal of attention is currently being paid to the synthesis of functionalized dihydropyrans.<sup>7-12</sup> 2,5-Bis(butylsulfanyl)-2,3-dihydro-4*H*-pyran-2-carbaldehyde is a compound which exhibits high antibacterial activity with low toxicity.<sup>13</sup>

There are few examples of reactions of these thio-substituted dihydropyrans described in the literature. For instance, some new Schiff bases were synthesized by the reaction of 2,5-bis(butylsulfanyl)-2,3-dihydro-4*H*-pyran-2-carbaldehyde with primary amines, as well as with amino acids and their esters.<sup>14</sup> The condensation of pyran **1** with 4-phenylthiosemicarbazide or thiosemicarbazide upon refluxing in EtOH afforded carbazones.<sup>15</sup> The synthesis of heterocycles from pyran **1** have not, so far, been implemented.

Herein, we report practical and simple methods to prepare linearly-coupled heterocyclic systems bearing a dihydropyran core in combination with oxazole, oxazoline or imidazolidine ring systems. It is known that five-membered nitrogen-containing heterocycles such as oxazole, oxazoline and imidazolidine are important scaffolds for a wide range of naturally-occurring and synthetic bioactive compounds, pharmaceuticals, and additional functionally-important materials.<sup>15-20</sup>

## Results and Discussion

In the present work, new heterocyclic compounds bearing 1,3-oxazole, 1,3-oxazoline and 1,3-imidazolidine moieties have been synthesized from 2,5-bis-(butylsulfanyl)-2,3-dihydro-4*H*-pyran-2-carbaldehyde.



**Scheme 1.** The reaction of 2,5-bis(butylsulfanyl)-2,3-dihydro-4*H*-pyran-2-carbaldehyde (**1**) with various nucleophiles.

It was demonstrated that pyran **1**, upon reflux with *p*-tosylmethyl isocyanide (TosMIC) in MeOH, in the presence of K<sub>2</sub>CO<sub>3</sub>, can be transformed into 1,3-oxazole **2** (Scheme 1a). These classical conditions of the Van Leusen reaction<sup>22</sup> turned out to be optimum for the formation of 1,3-oxazole **2** in 72% yield. Surprisingly, the reaction of pyran **1** with ethylisocyanoacetate in MeOH gave a trans-esterification product, 1,3-oxazoline **3a** (Scheme 1b). When ethanol was used instead of MeOH as a solvent, the target heterocycle **3b** was formed. The Et<sub>3</sub>N (1 equivalent) proved to be an effective catalyst in this reaction compared to those previously used in the literature.<sup>23</sup> Three chiral centers in compounds **3a,b** explains the presence of diastereomers and the doubling of signals in the NMR spectra (see online Supplementary Material). *N'*-Diphenylethylenediamine is added at the carbonyl group of pyran **1** to deliver 1,3-imidazolidine **4** in 93% yield (Scheme 1c). At room temperature, this reaction takes 12 days, while, upon heating, the duration to reaction completion is reduced to 8 hours.

The structures of compounds **2-4** were established by their NMR spectroscopy (<sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N) including 2D techniques. The <sup>15</sup>N NMR {<sup>1</sup>H-<sup>15</sup>N} HMBC spectra of product **4** shows cross-peaks of the nitrogen atom with CH proton, with ortho-protons of the Ph ring and CH<sub>2</sub> protons of the imidazolidine ring at -300.5 and -303.5 ppm, respectively.

## Conclusions

We have described a convenient route to the synthesis of linearly-coupled heterocyclic systems from 2,5-bis(butylsulfanyl)-2,3-dihydro-4*H*-pyran-2-carbaldehyde under mild conditions. The search for compounds with high biological activity with which to design efficient drugs represents a standing research challenge. In this effort, the syntheses of the above heterocyclic systems can be of valuable contributions to addressing this challenge.

## Experimental Section

**General.** The <sup>1</sup>H, <sup>13</sup>C and <sup>15</sup>N NMR spectra were recorded in CDCl<sub>3</sub> solutions at room temperature on Bruker DPX-400 and AV-400 spectrometers (400.13, 100.61 and 40.56 MHz), respectively). <sup>1</sup>H, <sup>13</sup>C and <sup>15</sup>N Chemical shifts (δ in ppm) were measured with accuracy of 0.01, 0.02 and 0.1 ppm, respectively, and referenced to TMS (<sup>1</sup>H, <sup>13</sup>C) and nitromethane (<sup>15</sup>N) internal standards. Chromato-mass spectrometry analysis was performed on a Shimadzu GCMS-QP5050A mass spectrometer (EI ionization, 70 eV). The IR spectra of the compounds were recorded on a Varian 3100 FT-IR spectrometer with the sample in thin film. Elemental analysis was performed on a Thermo Finnigan Flash series 1112 Elemental analyzer.

**5-[2,5-Bis(butylthio)-3,4-dihydro-2*H*-pyran-2-yl]-1,3-oxazole (**2**).** Synthesis of oxazole **2** was carried out according to the published procedure.<sup>24</sup> To a solution of aldehydes **1** (1 mmol) in a 6 ml of MeOH, was added TosMIC (1.1 mmol) and K<sub>2</sub>CO<sub>3</sub> (1.4 mmol). The reaction mixture was stirred for 3 h at 55-60 °C. The methanol was removed under vacuum, the residue was dissolved in ether, and the precipitate was filtered off. The ether was then removed, and the residue was purified by column chromatography (SiO<sub>2</sub>, eluent-chloroform). Yield 240 mg (72%). IR (n/cm<sup>-1</sup>): 2957, 2926, 2869, 2856, 1629, 1463, 1441, 1144, 1104, 1053, 828, 644. MR <sup>1</sup>H

(CDCl<sub>3</sub>):  $\delta$  = 0.84 (t, 3H, *J* 7.2 Hz, CH<sub>3</sub> (SBu)), 0.90 (t, 3H, *J* 7.3 Hz, CH<sub>3</sub> (SBu)), 1.25-1.59 (m, 8H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> (2SBu)), 2.12-2.42 (m, 4H, CH<sub>2</sub> at C-3' and C-4'), 2.50-2.60 (m, 4H, 2SCH<sub>2</sub>), 6.64 (s, 1H, H-4), 7.08 (s, 1H, =CH), 7.85 (s, H-2). MR <sup>13</sup>C (CDCl<sub>3</sub>):  $\delta$  = 13.7 (CH<sub>3</sub>), 13.8 (CH<sub>3</sub>), 21.7 (CH<sub>2</sub>CH<sub>3</sub> in SBu at C-2'), 22.1 (CH<sub>2</sub>CH<sub>3</sub> in SBu at C-5'), 24.0 (C-3'), 28.6 (C-4'), 31.5 (SCH<sub>2</sub>CH<sub>2</sub>), 31.6 (SCH<sub>2</sub>CH<sub>2</sub>), 32.4 (SCH<sub>2</sub>), 32.6 (SCH<sub>2</sub>), 82.6 (C-2'), 107.6 (C-5'), 124.1 (C-6'), 143.1 (C-4), 150.8 (C-2), 151.8 (C-5).

NMR <sup>15</sup>N = -125.3. GC-MS, *m/z* (%): 238 [M]<sup>+</sup>-SBu (35), 183 (10), 168 (19), 152 (7), 127 (100), 123 (6), 99 (8), 85 (23), 83 (27), 57 (21), 43 (24), 41 (77). Found (%): C, 58.38; H, 7.56; S, 19.22; N 4.02. Calculated C<sub>16</sub>H<sub>25</sub>S<sub>2</sub>O<sub>2</sub>N (%): C, 58.72; H, 7.64; S, 19.57; N, 4.28.

**Synthesis of oxazolines (3).** To a solution of aldehydes **1** (1 mmol) in a 6 ml of MeOH/EtOH, was added ethylisocynoacetate (1 mmol) and Et<sub>3</sub>N (1 mmol). The reaction mixture was refluxed for 2-6 h. The solvent was removed under vacuum, and the residue was purified by column chromatography (SiO<sub>2</sub>, eluent-chloroform).

**5-[2,5-Bis(butylthio)-3,4-dihydro-2H-pyran-2-yl]-4-methoxy-4,5-dihydro-1,3-oxazole (3a).** yield 313 mg (81%). NMR <sup>1</sup>H (CDCl<sub>3</sub>):  $\delta$  = 0.88-0.92 (m, 6H, 2CH<sub>3</sub> (SBu)), 1.33-1.48 (m, 4H, 2CH<sub>2</sub>CH<sub>3</sub> (SBu)), 1.51-1.55 (m, 4H, 2SCH<sub>2</sub>CH<sub>2</sub> (SBu)), 1.86-2.19 (m, 3H, CH<sub>2</sub> at C-3' and C-4'), 2.49-2.63 (m, 5H, 4H in 2SCH<sub>2</sub> and 1H in CH<sub>2</sub> at C-4'), 3.82 (s, 3H, OMe), 4.67 and 4.80 (two dd, 1H, *J* 2.1 Hz and *J* 7.1 Hz, H-4), 4.96 and 5.20 (two dd, 1H, *J* 7.1 Hz and *J* 2.1 Hz, H-5), 6.56 and 6.60 (two s, 1H, CH=), 6.91 and 6.94 (two d, 1H, *J* 2.1 Hz, H-2).

NMR <sup>13</sup>C (CDCl<sub>3</sub>):  $\delta$  = 13.1 (CH<sub>3</sub> (Bu)), 13.2 (CH<sub>3</sub> (Bu)), 21.2 (CH<sub>2</sub>CH<sub>3</sub> (SBu) at C-2'), 21.6 (CH<sub>2</sub>CH<sub>3</sub> (SBu) at C-5'), 22.9 (C-4'), 26.5 (C-3'), 27.7 (SCH<sub>2</sub> at C-2'), 31.1 (2SCH<sub>2</sub>CH<sub>2</sub>), 31.7 (SCH<sub>2</sub> at C-5'), 52.4 (OCH<sub>3</sub>), 68.5 (C-4), 84.0 (C-2'), 84.2 (C-5), 107.7 (C-5'), 142.3 (C-6'), 155.6 (C-2), 170.4 (C=O).

NMR <sup>15</sup>N = -154.9. GC-MS, *m/z* (%): 387 [M]<sup>+</sup> (6), 298 [M]<sup>+</sup>-SBu (6), 271 (7), 253 (37), 238 (9), 184 (7), 168 (5), 158 (53), 144 (6), 126 (26), 115 (9), 99 (14), 85 (20), 81 (24), 57 (42), 55 (35), 41 (100). Elemental analysis calcd for C<sub>18</sub>H<sub>29</sub>S<sub>2</sub>O<sub>4</sub>N: C, 55.81; H, 7.49; S, 16.54; N, 3.62. Found: C, 56.08; H, 7.26; S, 16.50; N 3.77.

**5-[2,5-Bis(butylthio)-3,4-dihydro-2H-pyran-2-yl]-4-ethoxy-4,5-dihydro-1,3-oxazole (3b).** Yield 332 mg (83%). IR (n/cm<sup>-1</sup>): 2958, 2930, 2160, 1741, 1630, 1462, 1270, 1198, 1147, 1104, 1047, 843, 746. NMR <sup>1</sup>H (CDCl<sub>3</sub>):  $\delta$  = 0.86-0.91 (m, 6H, 2CH<sub>3</sub> (SBu)), 1.30-1.43 (m, 7H, CH<sub>3</sub> (OEt), 2CH<sub>2</sub>CH<sub>3</sub> (SBu)), 1.43-1.54 (m, 4H, 2SCH<sub>2</sub>CH<sub>2</sub> (SBu)), 1.85-2.18 (m, 3H, CH<sub>2</sub> at C-3' and C-4'), 2.49-2.62 (m, 5H, 4H in 2SCH<sub>2</sub> and 1H in CH<sub>2</sub> at C-4'), 4.24-4.28 (m, 2H, OCH<sub>2</sub>), 4.63 and 4.76 (two dd, 1H, *J* 2.2 Hz and *J* 7.2 Hz, H-4), 4.95 and 5.17 (two dd, 1H, *J* 7.2 Hz and *J* 2.2 Hz, H-5), 6.55 and 6.59 (two s, 1H, CH=), 6.91 and 6.94 (two d, 1H, *J* 2.2 Hz, H-2).

NMR <sup>13</sup>C (CDCl<sub>3</sub>):  $\delta$  = 14.0 (CH<sub>3</sub> (Bu)), 14.1 (CH<sub>3</sub> (Bu)), 14.6 (CH<sub>3</sub> (OEt)), 22.1 (CH<sub>2</sub>CH<sub>3</sub> (SBu) at C-2'), 22.5 (CH<sub>2</sub>CH<sub>3</sub> (SBu) at C-5'), 23.82 (C-4'), 27.5 (C-3'), 28.6 (SCH<sub>2</sub>), 32.0 (2SCH<sub>2</sub>CH<sub>2</sub>), 32.7 (SCH<sub>2</sub> at C-5'), 62.4 (OCH<sub>2</sub>), 69.6 (C-4), 85.2 (C-5), 108.6 (C-5'), 143.3 (C-6'), 156.4 (C-2), 170.9 (C=O). NMR <sup>15</sup>N = -153.8. GC-MS, *m/z* (%): 401 [M]<sup>+</sup> (24), 356 (3), 312 (18), 267 (92), 238 (13), 228 (7), 211 (10), 200 (11), 184 (21), 172 (92), 155 (8), 144 (17), 126 (33), 112 (11), 99 (21), 85 (23), 71 (23), 57 (60), 55 (33), 41 (100). Calculated C<sub>19</sub>H<sub>31</sub>S<sub>2</sub>O<sub>4</sub>N (%): C, 56.86; H, 7.73; S, 15.96; N, 3.49. Found (%): C, 56.58; H, 7.51; S, 16.27; N 3.30.

**2-[(1Z)-1-(Butylthio)-4-phenylbut-1-en-3-yn-1-yl]-1,3-diphenylimidazolidine (4).** To a mixture of aldehydes **1** (1 mmol) in 5 ml EtOH was added *N,N'*-diphenylethylenediamine (1 mmol) and the mixture was stirred at 60 °C for 8 h. The reaction mixture was dried over MgSO<sub>4</sub> and filtered. The reaction mixture was refluxed for 8 h. Recrystallization from ethanol gave light yellow solid, mp. 148 °C. Yield 448 mg, 93%. IR (n/cm<sup>-1</sup>): IR: 2956, 2924, 1630, 1596, 1502, 1378, 1144, 1042, 995, 910, 747, 692. NMR <sup>1</sup>H (CDCl<sub>3</sub>):  $\delta$  = 0.86 (t, 3H, *J* 7.2 Hz, CH<sub>3</sub> (SBu)), 0.97 (t, 3H, *J* 7.3 Hz, CH<sub>3</sub> (SBu)), 1.29-1.61 (m, 6H, 2CH<sub>2</sub>CH<sub>3</sub> (SBu) and SCH<sub>2</sub>CH<sub>2</sub> at C-2'), 1.99-2.15 (m, 3H, CH<sub>2</sub> at C-3' and C-4'), 2.49-2.62 (m, 7H, 2SCH<sub>2</sub>(SBu) and SCH<sub>2</sub>CH<sub>2</sub> at C-5', C-4'), 3.68, 3.77, 3.83, 4.12 (4m, 4H, 2CH<sub>2</sub> in imidazolidine), 5.83 (s, 1H, CH), 6.64 (s, 1H, CH=), 6.78 (m, 2H, *p*-H in Ph), 6.86 (d, 2H, *o*-H in Ph, *J*

8.2 Hz), 6.98 (d, 2H, *o*-H in Ph, *J* 8.1 Hz), 7.26 (m, 4H, *m*-H in Ph). NMR <sup>13</sup>C (CDCl<sub>3</sub>): δ = 13.8 (CH<sub>3</sub> (Bu)), 13.8 (CH<sub>3</sub> (Bu)), 21.7 (CH<sub>2</sub>CH<sub>3</sub> in SBu at C-2'), 22.3 (CH<sub>2</sub>CH<sub>3</sub> in SBu at C-5'), 24.3 (C-4'), 28.9 (SCH<sub>2</sub> at C-2'), 29.5 (C-3'), 31.7 (SCH<sub>2</sub>CH<sub>2</sub>), 31.8 (SCH<sub>2</sub>CH<sub>2</sub>), 32.4 (SCH<sub>2</sub> at C-5'), 48.8 (NCH<sub>2</sub>), 49.3 (NCH<sub>2</sub>), 80.1 (CH), 91.0 (C-2'), 107.9 (C-5'), 113.6 and 114.3 (*o*-C in Ph), 117.8 and 118.3 (*p*-C in Ph), 129.1 (*m*-C in Ph), 143.0 (C-6'), 148.1 and 148.3 (C<sub>i</sub> in Ph). NMR <sup>15</sup>N (CDCl<sub>3</sub>): -300.5, -303.5. Found (%): C, 69.32; H, 7.71; S, 13.07; N 5.88. Calculated C<sub>28</sub>H<sub>38</sub>S<sub>2</sub>O<sub>1</sub>N<sub>2</sub> (%): C, 69.71; H, 7.88; S, 13.28; N, 5.81.

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## Supplementary Material

<sup>1</sup>H and <sup>13</sup>C NMR spectra are provided in a Supplementary Material file available on the publisher's website along with the published article.

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