



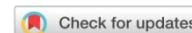
## Investigation on the thio-Claisen rearrangement of 2-[(4-aryloxy-2-butynyl)sulfanyl]thiophene

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**Abstract:** 2H-thiopyrano[3,2-c]coumarins have been regioselectively produced in 55-78% yield by the thermal [3,3] sigmatropic rearrangement led us to conduct research on the thio Claisen rearrangement of 2-[(4-aryloxy-2-butynyl)sulfanyl]thiophene. Six different cases using various 4-chlorobut-2-yne were subjected to [3,3] sigmatropic rearrangement. The first cyclization in every cases were successful. The products formed contain allyl aryl ether moiety and as such there was scope for the second Claisen rearrangement with the products. The first Claisen product with Ar = 3,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> has been successfully undergone double Claisen rearrangement. As double Claisen rearrangement requires higher activation energy, the selection of solvent and catalyst was very important. In this case, anhydrous AlCl<sub>3</sub>, BF<sub>3</sub>-etherate was successfully chosen to get the reaction completed within one hour with enhanced yield.

### Introduction

Claisen rearrangement (Ireland et al., 1972; Ito et al., 1997, 1999; Martín Castro, 2004; Thyagarajan, 1967; Ziegler, 1977, 1988) is a carbon-carbon bond-forming (Li, 1993; Lutz, 1984) chemical reaction, a [3,3] Sigmatropic rearrangement (Kurth et al., 1985; Lambert et al., 2002; Majumdar et al., 2001; Majumdar & Samanta, 2002; Majumdar et al., 2001). It has ushered in one of the pre-eminent construction procedures of carbon-carbon bonds in organic synthetic chemistry. Stereo control of the highest order can be achieved by the concerted [3,3] sigmatropic rearrangement (Majumdar et al., 2003, 2006), resulting in various new chemical compounds. It has opened up a new horizon in organic synthesis. The major application of Claisen rearrangement in the synthesis of various oxygen (Burns et al., 2018; Ito et al., 1999; Moody, 1987; Otter et al., 1972; Sankara-Subramanian et al., 1989; Ziegler, 1977, 1988) nitrogen (Kurth et al., 1985; Majumdar et al., 2001; Majumdar & Samanta, 2002; Moody, 1987; Thyagarajan, 1967) and sulphur (Anisimov et al., 1980; Majumdar et al., 2012; Majumdar et al., 2003; Morin et al., 1979) containing heterocyclic

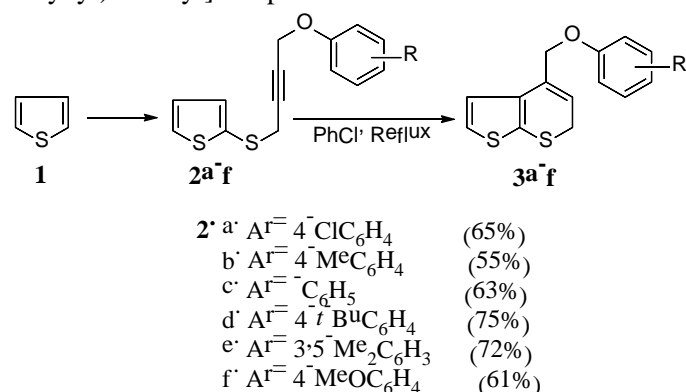
compounds has made this [3,3] sigmatropic rearrangement methodology more useful. As compared to oxy (Ito et al., 1999; Kirchner et al., 1988; Koreeda et al., 1985; Majumdar et al., 2008; Ziegler, 1977, 1988) and aza-Claisen rearrangements (Fischer et al., 2009; Jung et al., 2017; Majumdar et al., 2009; Nubbemeyer, 2005) little work has been done on the thio-Claisen rearrangement. (Eberhart, Cicoira, et al., 2013; Eberhart & Procter, 2013; Kwart et al., 1966; Majumdar et al., 2012; Morin et al., 1979; Yang et al., 2020)

Some important documentation is made (Majumdar et al., 2012; Majumdar et al., 2003; Majumdar & Ghosh, 2002) still there is enormous scope in this field. Thio-Claisen rearrangement can be used to make a variety of biologically relevant heterocyclic compounds. Here lies the scope and importance of aza, thio-Claisen rearrangement. Cutting edge research in making of the next generation synthetic drugs of course can utilize of thio-Claisen rearrangement.

### Result and Discussion

The regioselective synthesis of 2H-thiopyrano[3,2-c]

coumarins by the thermal [3,3] sigmatropic rearrangement (Majumdar & Ghosh, 2002) inspired us to investigate the thioClaisen rearrangement of 2-[(4-aryloxy-2-butynyl)sulfanyl] thiophene.



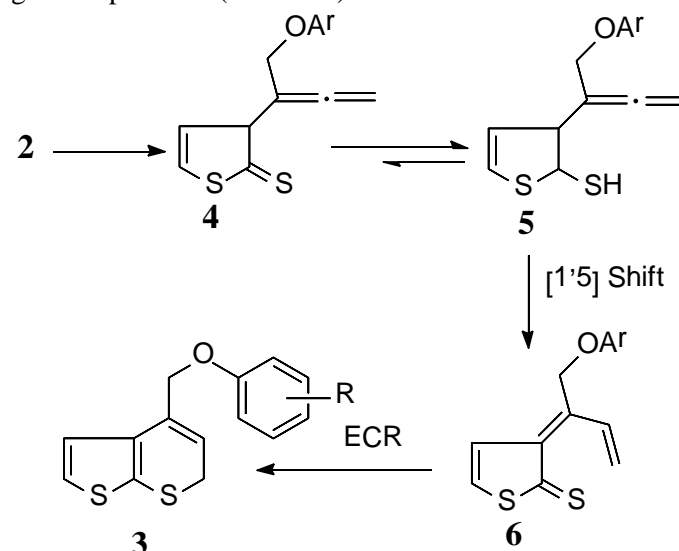
**Scheme 1. Synthesis of 3a-f from 1**

The starting materials for this study were made using a previously described process that combined commercially available thiophene 1 with different 4-chloro-but-2-ynes 2a-f. Compound 2a contains thienyl-propargyl moiety and is prone to thermal [3,3] sigmatropic rearrangement. TLC was used to monitor the reaction course as it was refluxed in chlorobenzene (b.p. 134°C). The compound's polarity remained unchanged, but the colour of the spot altered after exposure to iodine. The refluxing was continued for 8h, and the product 3a was obtained in 65% yield. UV, Mass, IR, and <sup>1</sup>H NMR spectroscopy were used to describe all of the substances. The <sup>1</sup>H NMR spectrum of the materials 3a presented a doublet at δ 3.53 as a doublet (*J* = 5.3 Hz) for -SCH<sub>2</sub> protons and a singlet at δ 4.72 for -OCH<sub>2</sub> protons. A one proton triplet appeared at δ 5.82 (*J* = 5.3 Hz) for the vinyl proton. The four protons of the phenyl ring appeared as two double doublets at δ 6.86 and δ 7.30 (*J* = 6.7, 2.1 Hz). Two thiophene protons appeared as a singlet at δ 7.05. The compound's mass spectrum revealed a molecular ion peak at *m/z* = 294, 296 (*M*<sup>+</sup>). This result has given us hope; therefore, we are going to keep going. The remaining substrates 2b-f were similarly treated to furnish the final compounds 3b-f in 55-75% yields (Scheme 1).

Despite the fact that substrates 2a-f have two potential sites for [3,3] sigmatropic rearrangement, an aryl-propargyl ether moiety and a thienyl-propargyl sulphide moiety, all of the substrates went through [3,3] sigmatropic rearrangement at the thienyl-propargyl sulphide moiety to give the compounds 3a-f.

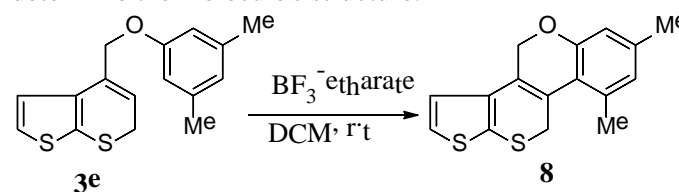
The production of 3a-f and 5 from 2a-f can be explained simply by the first [3,3] sigmatropic rearrangement of 2 to 4, followed by fast tautomerization to generate allenyl thiol 5. [1,5] Hydrogen shift in 5 yields 6,

which can then be closed with a 6-electrocyclic ring to get 3a-f products (scheme 2).



**Scheme 2. Synthesis of 3 from 2**

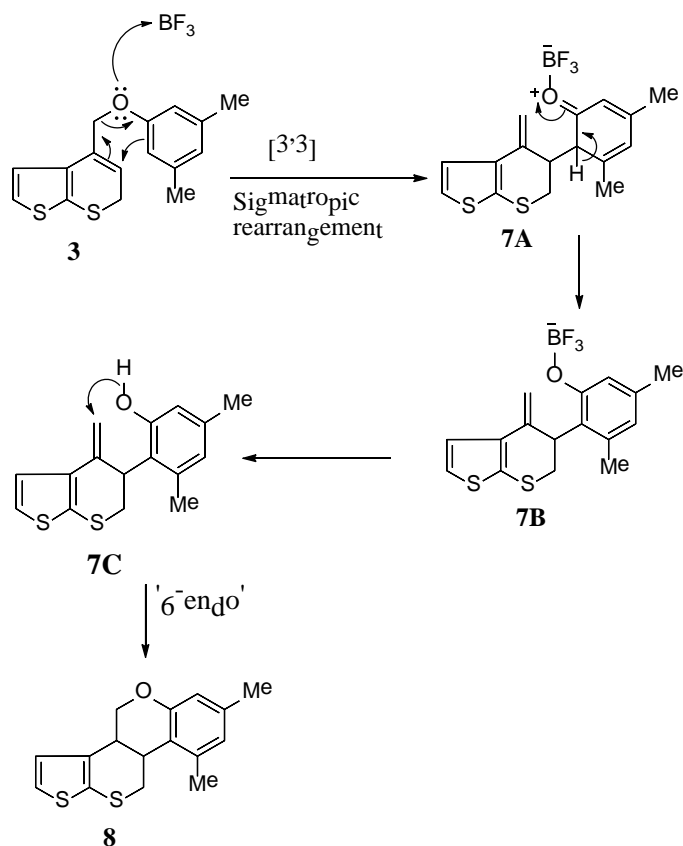
Compounds 3a-f also include an alkyl aryl ether moiety, according to a thorough inspection of the products. Because of this, there is scope for the second Claisen rearrangement to be implemented. Second Claisen rearrangement requires higher activation energy than that of the first due to the disturbance of aromaticity in the transition state. The compounds 3a-f in high boiling solvents like DMF, dichlorobenzene, *N,N*-dimethyl aniline and quinolines for 10- 15h gave no characterizable product. We also tried catalyzed Claisen rearrangement using anhydrous AlCl<sub>3</sub>, BF<sub>3</sub>-etherate etc. Only in case of compound 3e do we get the cyclized product. Compound 3e was treated with cat. amount of anhydrous BF<sub>3</sub>-etherate in DCM (Scheme 3) and as well as TLC, which was used to monitor the progress of the reaction. Within one hour, the entire conversion process was completed. But in other cases, we failed to obtain the desired cyclized products. The <sup>1</sup>H NMR spectroscopy of compound 8 was used to determine the molecule's structure.



**Scheme 3. Synthesis of 8 from 3e**

The proton NMR spectrum of the material 8 displayed two three-proton singlets at δ 1.81 and 2.28 due to two aromatic methyl groups. Two -SCH<sub>2</sub> protons looked as two triplets at δ 2.14 (*J* = 13.0 Hz) and 3.14 (*J* = 12.9 Hz) and ring junction protons looked as two multiplets at δ 2.30 and δ 2.98. Two one proton doublets at δ 4.33 (*J* = 9.0 Hz) and δ 4.38 (*J* = 9.0 Hz) showed the presence of

two  $-OCH_2$  protons. The two aromatic protons looked like two singlets at  $\delta$  6.48 and  $\delta$  6.53 whereas the two thiophene protons looked as two doublets at  $\delta$  6.69 and  $\delta$  6.98 ( $J = 5.2$  Hz). It is possible that substrate **3e** will form an etheroxygen- $BF_3$  complex that will go through [3,3] sigmatropic alteration through a charge delocalized transition state to give intermediate **7A**, which will then go through rapid tautomerization and proton exchange to give intermediate phenol **7C**, which will go through 6-endo-cyclization to give the products **8** (scheme 4).



Scheme 4. Synthesis of **8** from **3**

## Experimental Section

### General procedure for the preparation of compound 3a-f

Compounds **2a-f** (1.5 mmol) were cooked for 8 hours in refluxing chlorobenzene (5 ml) to achieve their final concentration. TLC was used to keep track of the response. The chlorobenzene was removed from the solution by elution of the column (Silica gel, 60-120 mesh) with petroleum ether (60- 80°C). The pure compounds **3a-f** were obtained after elution of the column with a 50:1 mixture of petroleum ether and ethyl acetate.

### 4-[(4-chlorophenoxy)methyl]-6Hthieno[2,3-b]thiopyran (**3a**)

Yield: 65%; Viscous liquid  
IR (Neat): 1493, 2923 $cm^{-1}$

UV (CHCl<sub>3</sub>)  $\lambda_{max}$  220, 278 nm

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300MHz):  $\delta$  3.50 (d,  $J = 5.3$  Hz, 2H, -SCH<sub>2</sub>), 4.72 (s, 2H, -OCH<sub>2</sub>), 5.82 (t,  $J = 5.3$  Hz, 1H, C=CH), 6.86 (dd,  $J = 6.7, 2.1$ Hz, 2H, ArH), 7.05 (s, 2H, Thiophene H), 7.30 (dd,  $J = 6.7, 2.1$ Hz, 2H, ArH)

MS:  $m/z = 294, 296$  ( $M^+$ )

Anal. Calcd for C<sub>14</sub>H<sub>11</sub>ClOS<sub>2</sub>: C, 57.03; H, 3.76; Found: C, 56.89; H, 3.95%.

### 4-[(4-methylphenoxy)methyl]-6Hthieno[2,3-b]thiopyran (**3b**)

Yield: 55%;

Viscous liquid IR (Neat): 1495, 2923 $cm^{-1}$

UV (CHCl<sub>3</sub>)  $\lambda_{max}$  : 222, 277 nm

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300MHz):  $\delta$  2.30 (s, 9H, ArMe), 3.50 (d,  $J = 5.3$  Hz, 2H, -SCH<sub>2</sub>), 4.72 (s, 2H, -OCH<sub>2</sub>), 5.83 (t,  $J = 5.3$  Hz, 1H, C=CH), 6.97-7.23 (m, 6H, ArH, Thiophene H)

MS:  $m/z = 274$  ( $M^+$ )

Anal. Calcd for C<sub>15</sub>H<sub>14</sub>OS<sub>2</sub>: C, 65.66; H, 5.14; Found: C, 65.38; H, 5.28%.

### 4-(phoxymethyl)-6H-thieno[2,3-b]thiopyran (**3c**)

Yield: 63%; Viscous liquid

IR (Neat): 1493, 2923 $cm^{-1}$

UV (CHCl<sub>3</sub>):  $\lambda_{max}$  : 220, 276 nm

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300MHz):  $\delta$  3.52 (d,  $J = 5.3$  Hz, 2H, -SCH<sub>2</sub>), 4.75 (s, 2H, -OCH<sub>2</sub>), 5.85 (t,  $J = 5.3$  Hz, 1H, C=CH), 6.95-7.00 (m, 3H, ArH), 7.04 (d,  $J = 5.3$  Hz, 1H, Thiophene H), 7.08 (d,  $J = 5.3$  Hz, 1H, Thiophene H), 7.30 (d,  $J = 8.7$  Hz, 2H, ArH)

MS:  $m/z = 260$  ( $M^+$ )

Anal. Calcd for C<sub>14</sub>H<sub>12</sub>OS<sub>2</sub>: C, 64.58; H, 4.65; Found: C, 64.35; H, 4.78%.

### 4-[(4-tert-butylphenoxy)methyl]-6Hthieno[2,3-b]thiopyran (**3d**)

Yield: 75%;

White Solid, m.p. 109°C IR (Neat): 1495, 2927 $cm^{-1}$

UV (CHCl<sub>3</sub>):  $\lambda_{max}$  : 220, 277 nm.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300MHz):  $\delta$  1.35 (s, 9H, -CMe<sub>3</sub>), 3.53 (d,  $J = 5.3$  Hz, 2H, -SCH<sub>2</sub>), 4.76 (s, 2H, -OCH<sub>2</sub>), 5.86 (t,  $J = 5.3$  Hz, 1H, C=CH), 6.92 (d,  $J = 8.8$  Hz, 2H, ArH), 7.05 (d,  $J = 5.3$  Hz, 1H, Thiophene H), 7.12 (d,  $J = 5.3$  Hz, 1H, Thiophene H), 7.33 (d,  $J = 8.8$  Hz, 2H, ArH) <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75MHz):  $\delta$  30.02, 34.0, 36.55, 72.06, 116.77, 117.51, 123.86, 126.78, 128.55, 128.74, 132.99, 135.17, 136.95, 146.77, 158.76

MS:  $m/z = 316$  ( $M^+$ )

Anal. Calcd for C<sub>18</sub>H<sub>20</sub>OS<sub>2</sub>: C, 68.31; H, 6.37; Found: C, 68.55; H, 6.12%.

**4-[(3,5-dimethylphenoxy)methyl]-6Hthieno[2,3-b]thiopyran (3e)**

Yield: 72%; Viscous liquid

IR (Neat): 1495, 2922cm<sup>-1</sup>UV (CHCl<sub>3</sub>): λ<sub>max</sub> : 221, 277 nm.<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300MHz): δ 2.29 (s, 6H, ArCH<sub>3</sub>), 3.50 (d, *J* = 5.4 Hz, 2H, -SCH<sub>2</sub>), 4.70 (s, 2H, -OCH<sub>2</sub>), 5.82 (t, *J* = 5.4 Hz, 1H, C=CH), 6.56-6.62 (m, 3H, ArH), 7.02 (d, *J* = 5.2 Hz, 1H, Thiophene H), 7.07 (d, *J* = 5.2 Hz, 1H, Thiophene H)MS: *m/z* = 288 (M<sup>+</sup>)Anal. Calcd for C<sub>16</sub>H<sub>16</sub>OS<sub>2</sub>: C, 66.63; H, 5.59; Found: C, 67.01; H, 5.27%.**4-[(4-methoxyphenoxy)methyl]-6Hthieno[2,3-b]thiopyran (3f)**

Yield: 61%; Viscous liquid

IR (Neat): 1493, 2926cm<sup>-1</sup>UV (CHCl<sub>3</sub>): λ<sub>max</sub> : 220, 277 nm<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300MHz): δ 3.53 (d, *J* = 5.3 Hz, 2H, -SCH<sub>2</sub>), 3.76 (s, 3H, -OCH<sub>3</sub>), 4.69 (s, 2H, -OCH<sub>2</sub>), 5.81 (t, *J* = 5.2 Hz, 1H, C=CH), 6.81-6.86 (m, 4H, ArH), 7.03 (d, *J* = 5.3 Hz, 1H, Thiophene H), 7.08 (d, *J* = 5.3 Hz, 1H, Thiophene H)MS: *m/z* = 290 (M<sup>+</sup>)Anal. Calcd for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub>: C, 62.04; H, 4.86; Found: C, 62.36; H, 5.07%.**The method for preparing compound 8**

Two drops of BF<sub>3</sub>-etherate were added to a solution of compound 3e in dry DCM (10 ml). At room temperature, the reaction mixture was stirred for 1 hour. The reaction mixture was added to crushed ice and extracted with DCM. The mixed extracts were washed with 20 mL water and 20 mL brine and dried (Na<sub>2</sub>SO<sub>4</sub>). The solvent was withdrawn, and the resulting viscous mass was chromatographed on silica gel with ethyl acetate: petroleum ether (1:99) as the eluant to obtain the product 8.

**Compound 8**

Yield: 78%, Colourless solid, m.p. 123°C

IR (KBr): 1498, 2915cm<sup>-1</sup>UV (CHCl<sub>3</sub>): λ<sub>max</sub> : 222, 270 nm.<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500MHz): δ 1.81 (s, 3H, ArCH<sub>3</sub>), 2.14 (t, *J* = 13.0 Hz, 1H, -SCH<sub>2</sub>), 2.28 (s, 3H, ArCH<sub>3</sub>), 2.30-2.34 (m, 1H, Ring junction proton), 2.98-3.02 (m, 1H, Ring junction proton), 3.14 (t, *J* = 12.9 Hz, 1H, -SCH<sub>2</sub>), 4.33 (d, *J* = 9.0 Hz, 1H, -OCH<sub>2</sub>), 4.38 (d, *J* = 9.0 Hz, 1H, -OCH<sub>2</sub>), 6.48 (s, 1H, ArH), 6.53 (s, 1H, ArH), 6.69 (d, *J* = 5.2 Hz, 1H, Thiophene H), 6.98 (d, *J* = 5.2 Hz, 1H, Thiophene H)MS: *m/z* = 288 (M<sup>+</sup>)Anal. Calcd for C<sub>16</sub>H<sub>16</sub>OS<sub>2</sub>: C, 66.63; H, 5.59; Found: C, 66.92; H, 5.32%.**Conclusion**

Under heat circumstances, it has been accomplished to prolong the thio-Claisen rearrangement for the molecules 2a-f successfully. Despite the fact that it appears to be straightforward, this technology exhibits a high degree of regioselectivity and is a highly efficient protocol for the synthesis of fused heterocycles. Fused heterocycles thus synthesized may have some medicinal properties. Of course, this is another very important area of research in the field of medicinal chemistry.

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