# A CONVENIENT PREPARATION OF STERICALLY CROWDED 1,9-DISUBSTITUTED DIBENZOTHIOPHENES AND 3,3'-DISUBSTITUTED DIARYL SULFIDES

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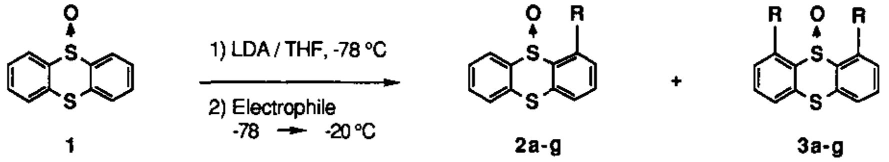
Abstract - Thianthrene-5-oxide (**1**) reacted with 2.2 equivalents of lithium diisopropylamide to give 4,6-dilithiated **1** which was converted to 4,6-disubstituted thianthrene-5-oxides (**3**). **3** afforded sterically crowded 1,9-disubstituted dibenzothiophenes (**4**) in moderate yields on treatment with n-butyllithium or phenyllithium.

Recently, we found that thianthrene-5-oxide (**1**) was converted to 2,2'-bis(1-aryl-1-hydroxymethyl)sulfides by treating initially with Grignard reagents and subsequently with aldehydes,[1] whereas Gilman reported that **1** gave dibenzothiophene by the reaction with n-butyllithium via ring contraction.[2] In order to utilize these substitution reactions of diaryl sulfoxides in organic synthesis, we examined the reaction of **1** with lithium diisopropylamide (LDA)[3,4] and subsequently with several electrophiles and found that **1** afforded 4,6-disubstituted thianthrene-5-oxides (**3a-g**) together with 4-monosubstituted compounds (**2a-g**). In this paper we report a convenient preparation of sterically crowded 1,9-disubstituted dibenzothiophenes (**4**) and 3,3'-disubstituted diphenyl sulfides (**5**) via the ligand coupling and ligand exchange reactions of **3**.

Typical reaction is as follows: **1** (232 mg, 1 mmol) in THF (5 ml) was lithiated with 0.44 M LDA (5 ml, 2.2 mmol) at -78 °C. To this solution was



(Eq. 1)

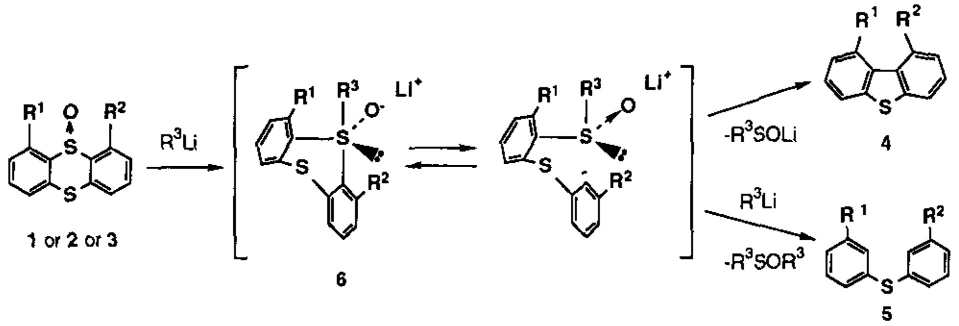
Table 1. Reaction of **1** with LDA and Electrophiles

| LDA(eq.) | Electrophile | R | Yield(%) | |
|---|---|---|---|---|
| | | | **2** | **3** |
| 1.1 | $(p\text{-TolS})_2$ | p-TolS | 66 (**2a**) | 21 (**3a**) |
| 2.2 | $(p\text{-TolS})_2$ | p-TolS | 26 (**2a**) | 53 (**3a**) |
| 1.1 | $(PhS)_2$ | PhS | 61 (**2b**) | 19 (**3b**) |
| 2.2 | $(PhS)_2$ | PhS | 25 (**2b**) | 61 (**3b**) |
| 1.1 | $(p\text{-ClC}_6H_4S)_2$ | $p\text{-ClC}_6H_4S$ | 55 (**2c**) | 26 (**3c**) |
| 2.2 | $(p\text{-ClC}_6H_4S)_2$ | $p\text{-ClC}_6H_4S$ | 29 (**2c**) | 38 (**3c**) |
| 2.2 | $S_8$ + MeI | MeS | 87 (**2d**) | trace (**3d**) |
| 3.3 | $S_8$ + MeI | MeS | trace (**2d**) | 63 (**3d**) |
| 2.2 | $(PhSe)_2$ | PhSe | 10 (**2e**) | 63 (**3e**) |
| 2.2 | PhCHO | PhCHOH | 77 (**2f**) | 0 (**3f**) |
| 2.2 | $Me_3SiCl$ | $Me_3Si$ | 4 (**2g**) | 65 (**3g**) |

added diphenyl disulfide (1.09 g, 5 mmol) in THF (5 ml). After usual work-up procedures and purification by column chromatography (silica gel; eluent, $CH_2Cl_2$) and then preparative liquid chromatography, 4-phenylthiothianthrene-5-oxide (**2b**) and 4,6-bis(phenylthio)thianthrene-5-oxide (**3b**) were obtained in 25 and 61% yields respectively.[5] Similarly, the lithiated **1** was treated with other electrophiles to give numerous 4- and 4,6-disubstituted thianthrene-5-oxides (**2-3**) (Eq. 1). The results are summarized in Table 1.

Furthermore, when the reactions of **2** and **3** bearing sulfenyl moieties were carried out using n-butyllithium or phenyllithium, both the ring contraction and ring opening reactions took place simultaneously affording the corresponding dibenzothiophenes (**4**) and diphenyl sulfide derivatives (**5**) (Eq. 2). The results are shown in Table 2.

Diaryl sulfoxides have never been known affording biaryl derivatives by the reactions with organometallic reagents. These reactions of 4,6-



(Eq. 2)

Table 2. Reactions of Substituted Thianthrene-5-oxides with Organolithium Reagents

| Run | Substrate | $R^1$ | $R^2$ | Yield (%) | | | |
|---|---|---|---|---|---|---|---|
| | | | | **4** | | **5** | |
| 1[a] | **3c** | $p$-ClC$_6$H$_4$S | $p$-ClC$_6$H$_4$S | 59 | (**4c**) | 30 | (**5c**) |
| 2[a] | **3b** | PhS | PhS | 65 | (**4b**) | 25 | (**5b**) |
| 3[b] | **3b** | PhS | PhS | 49 | (**4b**) | 17 | (**5b**) |
| 4[a] | **3a** | p-TolS | p-TolS | 46 | (**4a**) | 40 | (**5a**) |
| 5[a] | **3h** | PhS | MeS | 19 | (**4h**) | 35 | (**5h**) |
| 6[a] | **2b** | PhS | H | 10 | (**4j**) | 70 | (**5j**) |
| 7[b] | **2b** | PhS | H | 50 | (**4j**) | 45 | (**5j**) |
| 8[a] | **2a** | p-TolS | H | 10 | (**4i**) | 52 | (**5i**) |
| 9[a] | **3d** | MeS | MeS | 22 | (**4d**) | 65 | (**5d**) |
| 10[a] | **1** | H | H | 4 | (**4k**) | 42 | (**5k**) |
| 11[b] | **1** | H | H | 78 | (**4k**) | trace | (**5k**) |

[a] $R^3Li$ : n-butyllithium, [b] $R^3Li$ : phenyllithium.

disubstituted thianthrene-5-oxides (**3**) with organolithium reagents are attractive not only for investigating the mechanism of the coupling reactions of diaryl sulfoxides but also for providing the convenient preparation of various dibenzothiophene derivatives (**4**). The reactions should be initiated by the attack of organolithium on the sulfinyl sulfur atom to form the sulfurane (**6**) as an intermediate which gives **4** and **5** via the intramolecular ligand coupling or ligand exchange process.[6] Furthermore, the sulfoxides (**3a-c**) bearing arylthio substituents gave better yields of the coupling products than the methylthio derivative (**3d**) suggesting that the ligand coupling reaction of **3a-c** is favorable due to electronic stabilization of the intermediate, σ-sulfurane (**6**) by the presence of two electron withdrawing arylthio groups (Eq. 2).

Our present investigation provides convenient and simple procedures for preparation of sterically congested 1,9-dithiasubstituted dibenzothiophenes (**4**) which are hardly prepared by the common methods. Further studies are in progress in this laboratory.

## ACKNOWLEDGEMENT

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5. **2b**: mp 149-150 °C; $^1$H-nmr (CDCl3) δ 7.83-6.97 (m, 12H, Ar-H); ir (KBr) 1038 cm$^{-1}$; ms (m/z): 340 (M$^+$); Anal. Calcd for $C_{18}H_{12}OS_3$: C, 63.50; H, 3.55%. Found: C, 63.42; H, 3.49%.
   **3b**: mp 212.5-213.5 °C; $^1$H-nmr (CDCl3) δ 7.82-6.83 (m, 16H, Ar-H); ir (KBr) 1027 cm$^{-1}$; ms (m/z): 432 (M$^+$-16); Anal. Calcd for $C_{24}H_{16}OS_4$: C, 64.25; H, 3.59%. Found: C, 64.07; H, 3.62%.
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