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

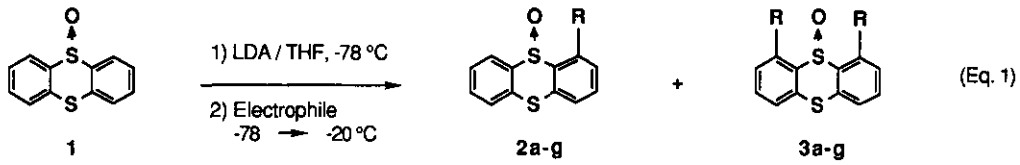


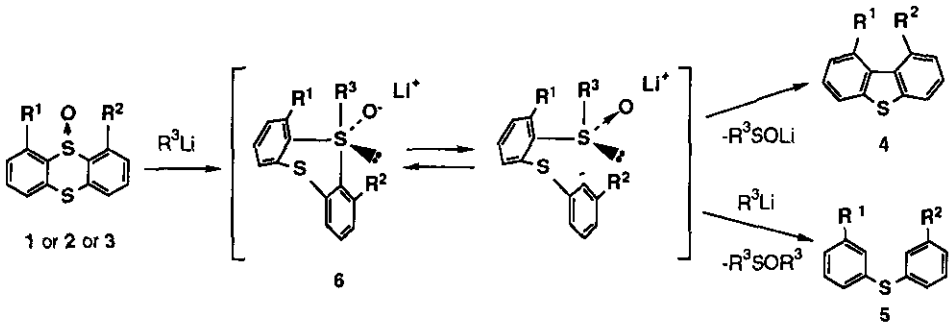
Table 1. Reaction of **1** with LDA and Electrophiles

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-phenylthio-thianthrene-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

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan (Grant No.02453018).

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5. **2b**: mp 149-150 °C; ^{1}H-nmr ($CDCl_3$) 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 ($CDCl_3$) 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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Received, 29th January, 1991