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ONE STEP SYNTHESIS OF POLYARYLTHIOETHERS CONSISTING OF ORTHO-PHENYLTHIO MOIETY

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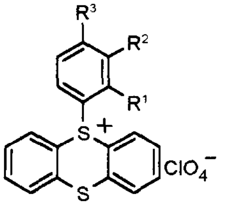
***Abstract*:** The reactions of 5-arylthianthrenium perchlorates with sodium hydrosulfide hydrate ($NaSH \cdot xH_2O$) in aqueous THF at reflux afforded polyarylthioethers having five sulfur atoms bonded to only ortho positions of each aryl group in good to excellent yields.

Recently we reported a convenient new method for the synthesis of bis(o-arylmercaptophenyl)sulfides (**2**) by the reactions of 5-arylthianthrenium perchlorates (**1**) with various thiolates in THF.[1] The compounds **2** cannot be prepared by the conventional method because of severe steric hindrance arising from bonding between ortho positions of each aryl groups.



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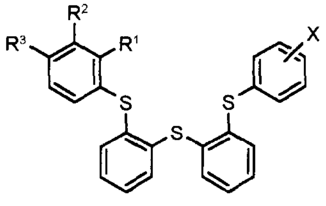

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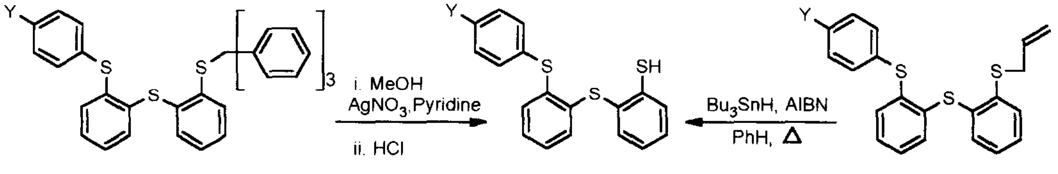
As a continuation of our studies dealing with utilization of **1**, we were in need to synthesize 2-mercaptophenyl 2'-(arylthio)phenyl sulfides (**3**) because the reactions of **1** with the thiolates of **3** might give polyarylthioethers having five sulfur atoms bonded to only ortho positions of each aryl group. Hydrolysis of 2-tritylthiophenyl 2'-arylthiophenyl sulfides (**4**)[2] according to the literature method[3] gave **3a** and **3b** in 65% and 32% yields, respectively. However, the reactions of **4** (Y = Me, MeO, EtO, NH_2) under the same conditions gave complex mixtures whose separation by chromatography was unsuccessful. The reactions of 2-allylthiophenyl 2'-arylthiophenyl sulfides (**5**) with Bu_3SnH by a radical mechanism[4] afforded **3c**, **3d**, and **3e** in 15%, 31%, and 11% yields, respectively.



4
a. Y = p-Me-$C_6H_4SO_2NH$
b. Y = MeCONH

3
a. Y = p-Me-$C_6H_4SO_2NH$
b. Y = MeCONH
c. Y = MeO
d. Y = EtO
e. Y = n-BuO

5
a. Y = MeO
b. Y = EtO
c. Y = n-BuO

Since those reactions tried gave unsatisfactory results in both of the yields of **3** and the separation of the reaction mixtures, we turned our attention to the reaction of **1** with sodium hydrosulfide hydrate ($NaSH \cdot xH_2O$) in aqueous THF.[5] The results are summarized in Table 1.

1

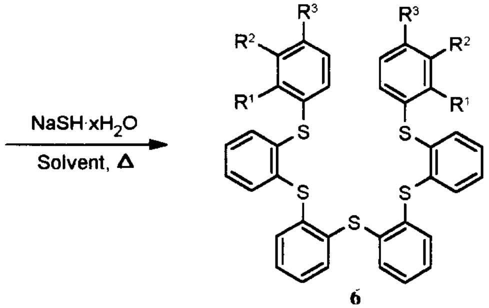


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Table 1. Synthesis of Symmetric Polyarylthioethers **6**.

entry	R^1	R^2	R^3	$NaSH \cdot xH_2O$ equiv†	solvent (v:v)	time h	yield,*% **6**
a	H	H	MeO	15	THF/H_2O (10:1)	21	90
				15	CH_3CN	19	83 (15)#
				15	PhH/H_2O (1:1)	48	81 (4)#
				8	PhH/H_2O (1:1)	20	61
				3	PhH/H_2O (1:1)	48	17 (5)#
				1	PhH/H_2O (1:1)	30	5 (8)#
				0.5	PhH/H_2O (1:1)	48	0
b	H	H	EtO	15	PhH/H_2O (1:1)	48	86
				15	CH_3CN	24	69 (10)#
c	H	H	n-BuO	15	PhH/H_2O (1:1)	21	99
d	H	H	MeCONH	15	PhH/H_2O (1:1)	40	13
				15	THF/H_2O (10:1)	22	79
e	H	$O—CH_2—O$		15	PhH/H_2O (1:1)	25	34 (8)#
				15	THF/H_2O (10:1)	22	93
f	H	H	Me	15	PhH/H_2O (1:1)	26	17 (22)#
				15	THF/H_2O (10:1)	24	75 (5)#
g	MeO	H	t-Bu	15	PhH/H_2O (1:1)	20	96
h	H	H	NH_2	15	PhH/H_2O (1:1)	37	37

*Isolated yield by column chromatography. All products were fully characterized by spectroscopic methods (^1H NMR, IR and mass spectrometry) and microanalysis. †Number of equivalent was calculated based on the formular NaSH. #Number in the parenthesis represents the yield of thianthrene. Compounds **1** are slightly soluble in aqueous THF and sparingly soluble in aqueous PhH at room temperature but disappear as the reactions proceed.

It is conceived that the compounds **6** are formed via the formations of their thiols **3** by sulfurane mechanism. However, no thiols were detected even in use of the low concentration of NaSH·xH_2O in which **1** was recovered quantitatively or the yield of **6** decreased drastically (entry **a**). In addition, treatment of a mixture of equimolar amounts of **1d** (R^3 = MeCONH) and **1** (R^3 = RO) with NaSH·xH_2O for 40 h under the same conditions gave two symmetric polyarylthioethers **6** and an unsymmetric polyarylthioether **7** as summarized in Table 2.

Table 2. Reactions of A Mixture of Equimolar Amounts of Two Different 5-Arylthianthrenium Perchlorate with NaSH·xH_2O.

reactants*		products (%)†		
1a (R^3 = MeO),	**1d**,(R^3 = MeCONH)	**6a** (45),	**6d** (47),	**7a**(53)
1b (R^3 = EtO),	**1d**,(R^3 = MeCONH)	**6b** (43),	**6d** (43),	**7b** (57)
1c (R^3 = n-BuO),	**1d**,(R^3 = MeCONH)	**6c** (50),	**6d** (44),	**7c** (50)

*R^1 = R^2 = H for **1a** - **d**. †Isolated yield by column chromatography. Examples for the calculations of the yields: Percent yield of **6a** = (No. of mmol of **6a**) × 2 × 100 / No. of mmol of **1a**. Percent yield of **7a** = No. of mmol of **7a** ×100 / No. of mmol of **1a**. All products were fully characterized by spectroscopic methods (^1H NMR, IR, and mass spectrometry) and microanalysis. **7a** (R^2 = H, R^3 = MeO ,Y = MeCONH); **7b** (R^2 = H, R^3 = EtO, Y = MeCONH); **7c** (R^2 = H, R^3 = n-BuO, Y = MeCONH). The order of R_f values (silica gel, EtOAc): **6a - c** > **7a - c** > **6d**.

The result indicates clearly the formations of two kinds of thiols, which lose protons under the basic conditions to form thiolates, followed by participation in the formations of sulfuranes, yielding **6** and **7**. The data also shows that little selectivity is involved in the reactions of these pairs of 5-arylthianthrenium salts with either NaSH·xH_2O or thiolates formed during the course of the reaction. On the other hand, treatment of **1** (R^1 = H) with independently synthesized thiolates of **3** in THF gave unsymmetric polyarylthioethers **7** in excellent yields. The results are summarized in Table 3.

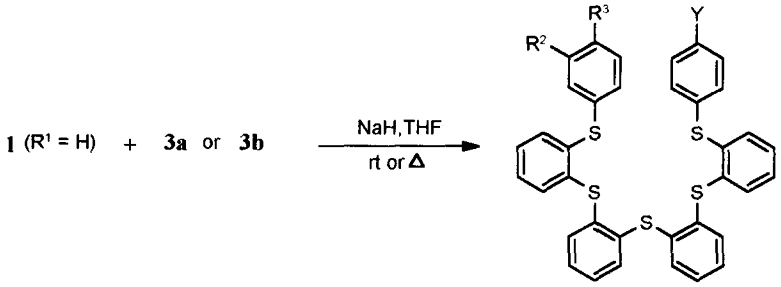

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Table 3. Sythesis of Unsymmetric Polyarylthioethers 7.

entry	R^2	R^3	Y	temp	time h	yield,*% 7
a	H	MeO	MeCONH	reflux	2.5	67
d	H	MeO	p-Me-$C_6H_4SO_2NH$	rt	8	86
e	H	EtO	p-Me-$C_6H_4SO_2NH$	rt	8	88
f	H	n-BuO	p-Me-$C_6H_4SO_2NH$	rt	8	88
g	H	i-PrO	p-Me-$C_6H_4SO_2NH$	rt	6.5	93
h	O—CH_2—O		p-Me-$C_6H_4SO_2NH$	rt	6	86
i	H	Me	p-Me-$C_6H_4SO_2NH$	rt	8	76
j	H	p-Me-$C_6H_4SO_2NH$	p-Me-$C_6H_4SO_2NH$	rt	2.5	96
k	H	MeCONH	p-Me-$C_6H_4SO_2NH$	reflux	1.5	37†

*Isolated yield by column chromatography. All products were fully characterized by spectroscopic methods (^{1}H NMR, IR, and mass spectrometry) and microanalyses. †The compound **7l** (R^2 = H, R^3 = MeO, Y = NH_2) was isolated as a major compound (58%) in addition to **7k**.

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REFERENCES AND NOTES

1. K. Kim and H. J. Rim, *Tetrahedron Lett.*, **1990**, *31*, 5631 - 5632.
2. Refer to reference 1 for the synthesis of 4.
3. L. Zervas and I. Photaki, *J. Am. Chem. Soc.*, **1962**, *84*, 3887-3897.
4. Y. Ueno and M. Okawara, *J. Am. Chem. Soc.*, **1979**, *101*, 1893-1894.
5. General procedure : To a stirred solution of 5-(p-anisyl)thianthrenium perchlorate (467 mg, 1.104 mmol) in THF (70 mL) was added NaSH·xH_2O (863 mg), followed by addition of water (7 mL), which was refluxed for 21 h. After the solvent was removed under vacuo, the residue was chromatographed on silica gel (Merck, 70-230 mesh). Thianthrene was removed by the elution with n-hexane. Elution next with chloroform gave 6a (338 mg, 0.498 mmol, 90%), recrystallized from n-hexane-ethyl acetate: mp 72-74°C ; ^{1}H NMR ($CDCl_3$, 80 MHz) δ 3.80 (s, 6H, MeO), 6.80-7.67 (m, 24H, ArH); IR (neat) 3050, 2900, 2850, 1600, 1500, 1450, 1300, 1250, 1190, 1120, 1050, 920, 850, 750 cm^{-1}; MS (m/e) 678 (M^+). Anal. Calcd for $C_{38}H_{30}O_2S_5$: C, 67.22; H, 4.45; S, 23.61. Found: C, 67.03; H, 4.59; S, 23.68.

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