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Synthesis of thieno[3,4-*d*]-1,3-dithiol-2-one derivatives

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ABSTRACT

A series of mono-substituted and bis-substituted derivatives of thieno [3,4-*d*]-1,3-dithiol-2-one were prepared through halogenation, chloromethylation, and subsequent nucleophilic substitution reactions. Compounds were characterized by NMR, FT-IR, and HRMS.

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1. Introduction

Polythiophene and its derivatives are of great interest as conductive polymers owing to their characteristic electrochemical, electronic, and optical properties.[1] The potential commercial applications include light-emitting diodes, smart windows, photovoltaic devices, and field effect transistors (FETs).[2] It has been recognized that the electrical and optical properties strongly depend on their structures. Recently, much attention has been focused on development of thiophene-based metallopolymers.[3] Thieno[3,4-*d*]-1,3-dithiol-2-one (**1**) emerged as a possible building block for synthesis of 2-D conductive metallopolymer or complex owing to its unique structure and ease of converting into dithiolate ligands under basic conditions to form metal-bis-dithiolene complex;[4] Another important aspect of the compound is the possibility of forming tetrathiafulvalene (TTF) or 2-thieno[3,4-*d*]-1,3-dithiol-2-ylidene-thieno[3,4-*d*]-1,3-dithiole (dithiophene-tetrathiafulvalene, DTTTF) like compounds through direct coupling. TTF charge-transfer salts are well known as good candidates for superconductive materials.[5,6] Therefore, the functionalization of **1** to afford key monomers for either cross-coupling polymerization[7] or two-step precursor polymerization[8–12] becomes a crucial step in the process of searching high-performance conductive polymers.

We report here synthesis of a series of thieno[3,4-*d*]-1,3-dithiol-2-one derivatives through halogenation, chloromethylation, and subsequent nucleophilic substitution reactions. All functionalization reactions occurred at 4 and/or 6 position(s) to maintain the annulated structure of thieno[3,4-*d*]-1,3-dithiol-2-one. These compounds might be good candidates to prepare conjugated polythiophene derivatives and/or thiophene-base metallopolymers.

2. Results and discussion

Compound **1** was prepared by oxidation of thieno[3,4-*d*]-1,3-dithiole-2-thione with mercury(II) acetate, in less than 20% overall yield.[13] A modified one-pot method based on the literature was used in our laboratory and gave a 48% yield from 3,4-dibromothiophene as starting material.[13–15]

Halogenation reaction of compound **1** with mild halogenated reagents such as *N*-chlorosuccinimide (NCS), *N*-bromosuccinimide (NBS), and *N*-iodosuccinimide (NIS), can selectively functionalize the 4 and/or 6 positions and give a variety of halogenated products with fairly good yields and stability (Scheme 1). Results of these reactions are listed in Table 1. Dibrominated compound **2d** was reported by direct bromination reaction of compound **1** with Br_2 in carbon tetrachloride, which afforded 95% yield.[16] Diiodinated compound **2f** could be synthesized through a two-step procedure, which involves treating compound **1** with mercury acetate at room temperature to give 4,6-diacetoxymercuri-thieno[3,4-*d*]-1,3-dithiol-2-one (compound **2g**), followed by iodination in dry acetonitrile to afford **2f** with an overall yield of 60% after column purification.

Among all bifunctional thiophene derivatives, 2,5-bis(chloromethyl)thiophene is regarded as a useful key compound toward

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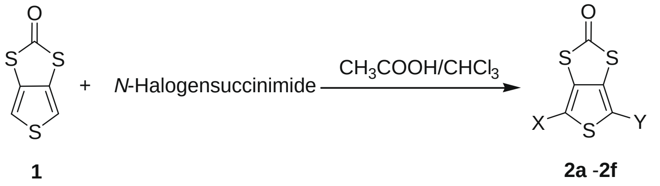
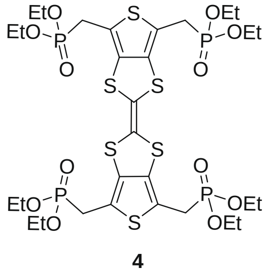


Scheme 1. General procedure to prepare halogenated derivatives of thieno[3,4-*d*]-1,3-dithiol-2-one.

Table 1
Halogenated derivatives of thieno[3,4-*d*]-1,3-dithiol-2-one (**1**)

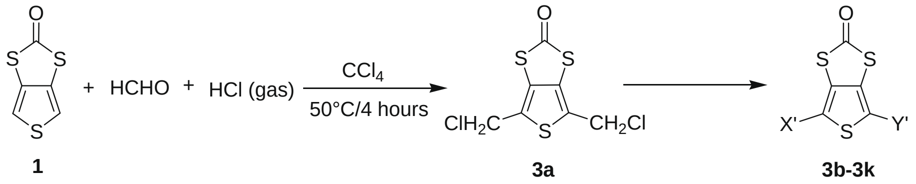
Compound	X	Y	Yield (%)	Mp (°C)
2a	Cl	H	72	95–96
2b	Cl	Cl	84	112–113
2c	Br	H	81	100–101
2d	Br	Br	87	130–131
2e	I	H	68	114–115
2f	I	I	82	185–186



Scheme 3. 4,4′,6,6′-Tetra(diethoxyphosphorylmethyl)-2-(thieno[3,4-*d*]-1,3-dithiol-2-ylidene)thieno[3,4-*d*]-1,3-dithiole.

the formation of various 2,5-bis-substituted thiophenes.[17,18] The chloromethylation reaction of thieno[3,4-*d*]-1,3-dithiol-2-one (**1**) proceeded similarly as the chloromethylation of thiophene, and afforded 4,6-bis(chloromethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (**3a**) with good yields (58%). It can be readily converted into other functionalized derivatives via nucleophilic reactions (Scheme 2). Nucleophilic substitution reactions were explored in transformation of **3a** into various derivatives having different functional groups, the results are summarized in Table 2. The coupling reaction of **3a** with triethyl phosphite gave an unique compound 4,4′,6,6′-tetra(diethoxyphosphorylmethyl)-2-(thieno[3,4-*d*]-1,3-dithiol-2-ylidene)thieno[3,4-*d*]-1,3-dithiole (**4**) in 32% yield. The compound possesses a core structure of DTTTF, which is shown in Scheme 3.

In summary, we have demonstrated the synthesis of thieno [3,4-*d*]-1,3-dithiol-2-one derivatives through halogenation, chloromethylation, and nucleophilic substitution reactions. The successful synthesis of these thiophene-based entities might lead to preparation of some unique conductive polymers, metallopolymers, and/or TTF-system materials. The study of polymerization of these derivatives to obtain conjugated conductive materials is still under investigation in our lab. The results will be reported in a timely manner.



Scheme 2. Synthesis of 4,6-bis(chloromethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (**3a**) and its derivatives.

Table 2
4,6-Bis(chloromethyl)thieno[3,4-*d*]-1,3-dithiol-2-one (**3a**) and its nucleophilic derivatives

Compound	X′	Y′	Yield (%)	Mp (°C)
3a	$-\mathrm{CH_2Cl}$	$-\mathrm{CH_2Cl}$	57	108–113 (decomposed)
3b	$-\mathrm{CH_2OH}$	$-\mathrm{CH_2OH}$	91	105–106
3c	$-\mathrm{CHO}$	$-\mathrm{CHO}$	82	215–216
3d	$-\mathrm{CH_2N(CH_2CH_3)_2}$	$-\mathrm{CH_2N(CH_2CH_3)_2}$	37	N/A (amber oil)
3e	$-\mathrm{CH_2Py^+(Cl^-)}$	$-\mathrm{CH_2Py^+(Cl^-)}$	95	>250
3f	$-\mathrm{CH_2OAc}$	$-\mathrm{CH_2OAc}$	68	119–120
3g	$-\mathrm{CH_2OCH_3}$	$-\mathrm{CH_2OCH_3}$	60	54–55
3h	$-\mathrm{CH_2SC(S)OCH_2CH_3}$	$-\mathrm{CH_2SC(S)OCH_2CH_3}$	97	98–100
3i	$-\mathrm{CH_2SC(S)N(CH_2CH_3)_2}$	$-\mathrm{CH_2SC(S)N(CH_2CH_3)_2}$	85	N/A (amber gel)
3j	$-\mathrm{CH_2P^+(Ph)_3(Cl^-)}$	$-\mathrm{CH_2P^+(Ph)_3(Cl^-)}$	95	>250
3k	$-\mathrm{CH_2SPh}$	$-\mathrm{CH_2SPh}$	75	94–96
3l	$-\mathrm{CH_2S(O)Ph}$	$-\mathrm{CH_2S(O)Ph}$	78	183–184
3m	$-\mathrm{CH_2SPh}$	$-\mathrm{CH_2S(O)Ph}$	83	152–154
3n	$-\mathrm{CH_2Cl}$	$-\mathrm{CH_2OAc}$	38	88–89
3o	$-\mathrm{CH_2Cl}$	$-\mathrm{CH_2OS(O)Ph}$	68	136–137

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Supplementary data

Supplementary data (detailed experimental procedures and NMR spectra of all new compounds) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.03.225.

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