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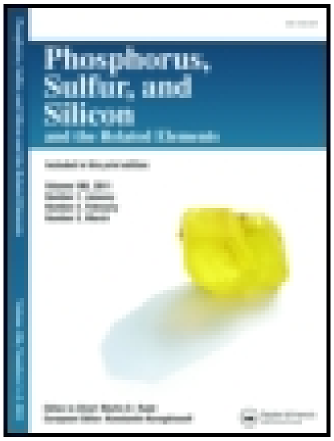

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A Novel Synthesis of Cyclic Polythioethers Using Liquid-Liquid Phase-Transfer Catalysis

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A NOVEL SYNTHESIS OF CYCLIC POLYTHIOETHERS USING LIQUID-LIQUID PHASE-TRANSFER CATALYSIS

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The synthesis of cyclic polythioethers has been achieved by the reactions of dithiols with alkyl dihalides. Thiols are not only hard to handle owing to their unpleasant smell, but also they are easily oxidizable, thus it is not easy to obtain various dithiols. However, we have developed a procedure for the preparation cyclic polythioethers by the reaction of dithioiminium salts with alkyl dihalides using phase-transfer catalyst without the use of dithiols, and have examined the ion recognition of these compounds.

Keywords: Cyclic polythioether; phase-transfer catalysis; thioacetamide; thiocrown; thioiminium salt

Many different methods for preparing cyclic polythioethers have been reported,[1–22] and they are known to favor their complexing ability with soft Lewis acids[4–9,23–29] because the sulfur atoms in the thioether groups are acting as soft Lewis bases. In addition, they have been shown to be effective ligands for low-valent transition metal ions,[30–33] whereas crown ethers prefer to coordinate alkaline and alkaline earth metal ions.[34–38] However, the coordination chemistry studies of cyclic polythioethers have progressed slowly owing to their lack of availability,[22] and the low yields obtained by conventional methods for their preparation.[30,31]

We have previously reported[39,40] an efficient method of synthesizing sulfides and thiol esters using 1-(alkylthio) or 1-(acylthio)ethaniminium halides as a source of alkanethiolate or thiocarboxylate ions. In an

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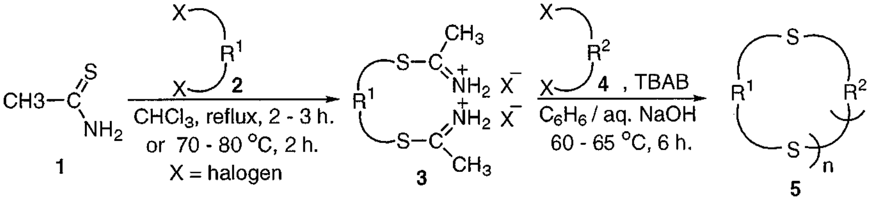
extension of this work, this article describes a novel and efficient method for the synthesis of cyclic polythioethers using the reaction of 1,1′-(dithioalkane)diethaniminium salts which are utilized to generate a variety of otherwise unavailable dithiolate ions. These react with alkyl dihalides under phase-transfer conditions.

RESULTS AND DISCUSSION

The reaction of alkyl dihalide (**2**) with two-fold excess of thioacetamide (**1**) afforded 1,1′-(dithio-alkane)diethaniminium salt (**3**) in refluxing chloroform for 2–3 h or at 70–80°C for 2 h without any solvent. The yields of **3** range between 70–90%.

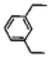
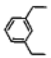


SCHEME 1

Alkyl dihalide (**4**) is added dropwise to a vigorously stirred reaction mixture containing 1,1′-(dithioalkane)diethaniminium salt (**3**) in a two-phase system consisting of benzene and an aqueous solution of sodium hydroxide at 60–65°C for 6 h in the presence of tetrabutylammmonium bromide (TBAB) as a phase-transfer catalyst. After the reaction is over, the organic phase is analyzed by gel permeation chromatography (GPC) using chloroform as an eluent. The main products of this reaction were cyclic polythioethers (**5**) and linear polymers having sulfur atoms. Two types of cyclic polythioethers (**5**) were obtained; 1:1 ratio (n = 1) and the 2:2 ratio (n = 2) which were separated by column chromatography on silica gel using hexane/EtOAc (9:1) as an eluent. The reaction did not proceed in the absence of a phase-transfer catalyst under otherwise identical conditions. The yields and physical properties of the cyclic polythioethers are summarized in Table I.

The yields for the cyclic polythioethers depend on the kind of alkali cations in the aqueous phase. While, the reaction time and the alkali concentration of the aqueous solution exhibit only a slight dependence on the yield. The reaction of **3** ($R^1 = (CH_2)_4$) with **4** ($R^2 = (CH_2)_4$) in a benzene/30% aqueous sodium hydroxide system produces 1:1 stoichiometrical product **5g**, dithio-10-crown-2, and 2:2 stoichiometrical product **5h**, tetrathio-20-crown-4, in 8 and 14% yield respectively. The use

TABLE I Yields and Physical Properties of Cyclic Polythioether **5**

5	R^1	R^2	n	yield[a] (%)	m.p. (°C)	HR-MS (El)[c] *m/z* (M$^+$)	HR-MS (El)[c] Unit	^{13}C-NMR (CDCl$_3$/TMS)[d] δ (ppm)
a	(CH$_2$)$_3$	(CH$_2$)$_2$	1	8	45–47	134.0216	$C_5H_{10}S_2$	31.8, 32.7, 38.6
b			2	10	118–119	268.0458	$C_{10}H_{20}S_4$	30.1, 30.4, 31.7
c	(CH$_2$)$_3$	(CH$_2$)$_3$	1	37	oil	148.0377	$C_6H_{12}S_2$	30.2, 30.8
d			2	10	51–53	296.0780	$C_{12}H_{24}S_4$	29.6, 30.7
e	(CH$_2$)$_4$	(CH$_2$)$_3$	1	22	56–58	162.0531	$C_7H_{14}S_2$	21.7, 25.9, 28.8, 32.2
f			2	24	59–60	324.1075	$C_{14}H_{28}S_4$	28.4, 29.7, 30.6, 31.5
g	(CH$_2$)$_4$	(CH$_2$)$_4$	1	8 (2)[b]	90–92	176.0679	$C_8H_{16}S_2$	25.5, 31.5
h			2	14 (17)[b]	31–32	352.1383	$C_{16}H_{32}S_4$	28.3, 31.3
i			3	–(5)[b]	71–73	528.2066	$C_{24}H_{48}S_6$	28.7, 31.6
j	(CH$_2$)$_6$	(CH$_2$)$_6$	1	12	78–79	232.1320	$C_{12}H_{24}S_2$	25.6, 27.2, 30.1
k			2	22	71–73	464.2636	$C_{24}H_{48}S_4$	28.5, 29.6, 32.1
l	(CH$_2$)$_8$	(CH$_2$)$_4$	1	10	65–67	232.1300	$C_{12}H_{24}S_2$	25.5, 26.7, 27.0, 29.8, 30.3
m			2	9	47–48	464.2634	$C_{24}H_{48}S_4$	28.5, 28.6, 28.9, 29.6, 31.6, 32.0
n	(CH$_2$)$_8$	(CH$_2$)$_8$	1	25	51–52	288.1925	$C_{16}H_{32}S_2$	27.7, 27.8, 29.0, 31.0
o			2	9	53–56	576.3847	$C_{32}H_{64}S_4$	28.7, 29.1, 29.5, 32.1
p	(CH$_2$)$_{10}$	(CH$_2$)$_5$	1	21	69–71	274.1768	$C_{15}H_{30}S_2$	27.1, 27.5, 27.6, 29.1, 29.4, 31.9, 32.0
q			2	4	57–59	548.3569	$C_{30}H_{60}S_4$	28.0, 28.7, 29.0, 29.2, 29.3, 29.7, 31.9, 32.1
r	(CH$_2$)$_{10}$	(CH$_2$)$_{10}$	1	19	48–50	344.2557	$C_{20}H_{40}S_2$	28.1, 28.5, 28.8, 29.3, 31.4
s			2	18	70–72	688.5156	$C_{40}H_{80}S_4$	29.0, 29.2, 29.5, 29.7, 32.2
t			1	9	120–121	272.0702	$C_{16}H_{16}S_2$	37.8, 127.0, 128.5, 131.8, 137.0
u			2	18	92–94	544.1356	$C_{32}H_{32}S_4$	39.1, 127.3, 129.1, 132.1, 138.0

[a] The yield is based on dithioiminium halides 3.

[b] Parentheses refer to the case of using aq. CsOH, otherwise aq. NaOH was used.

[c] Recorded on a Hitachi M-80B spectrometer.

[d] Obtained on a JEOL GX-400 spectrometer.

of cesium hydroxide in place of sodium hydroxide increases the yield of 2:2 stoichiometrical product **5h** (17%), together with a decrease of the 1:1 stoichiometrical product **5g** (2%), and a small amount of 3:3 stoichiometrical product **5i** (5%), hexathia-30-crown-6, as a new product. Similarly, the reaction of **3** ($R^1 = (CH_2)_3$) with **4** ($R^2 = (CH_2)_3$) in a benzene/sodium or potassium hydroxide system produces the 1:1 stoichiometrical compound **5c** as the main product but the similar reaction in a benzene/rubidium or cesium hydroxide system affords the 2:2 stoichiometrical compound **5d** as the main product.

These results show that the unit number (n) of cyclic polythioether increases with an increase in the ionic radius of alkali cation. The alkali cation plays an important role as a template in the formation of cyclic polythioethers (**5**). The extractability of alkali, transition and heavy metal ions by the cyclic polythioethers was evaluated,[36] and typical results are summarized in Table II.

All of the 2:2 stoichiometric products show a high selectivity toward Ag^+, but the 1:1 stoichiometric product shows only about half the extractability of 2:2 product. Cyclic polythioethers **5b**, **5d**, **5f**, and **5h** have 20 to 50% extractability for ions other than Ag^+ and **5k** to **5u** show only a weak extractability except for Ag^+ ion.

As far as we know, this is the first example of the synthesis of cyclic polythioethers in sulfur chemistry using 1,1′-(dithioalkane) diethaniminium salts. This method does not use malodorous

TABLE II Extraction of Alkaline, Transition Metal and Heavy Metal Ions

	Extraction (%)[a]								
Host	Li^+	Na^+	K^+	Co^{2+}	Ni^{2+}	Cu^{2+}	Ag^+	Cd^{2+}	Pb^{2+}
5g	4.2	2.6	5.2	2.6	0.9	2.8	44	5.0	4.8
5l	2.0	5.6	2.9	2.2	2.9	3.8	66	3.6	2.4
5b	1.7	3.8	20	7.6	20	8.4	99	28	22
5d	23	2.9	4.5	6.2	6.8	5.8	99	6.0	5.0
5f	6.8	4.1	8.3	6.6	50	5.4	98	7.0	9.0
5h	1.3	1.8	8.4	17	5.0	36	99	2.0	3.0
5k	2.2	1.3	2.5	3.0	3.0	8.4	99	11	6.0
5m	3.9	8.9	3.9	5.8	7.4	6.4	92	9.2	6.0
5o	1.1	2.0	3.4	3.0	3.6	4.4	98	4.8	6.1
5q	2.2	6.0	4.9	4.8	9.0	11	91	12	13
5s	4.1	7.2	3.8	6.2	5.4	4.4	97	5.0	5.2
5u	1.5	1.4	1.9	2.8	2.6	6.6	96	3.0	5.2
None	0.6	0.7	1.5	1.5	1.1	1.4	1.8	0.6	1.8

[a] Org. phase: (CH_2ClCH_2Cl); [Host] $= 3.0 \times 10^{-4}$ M; Aq. phase: [Pic^-H^+] $= 3.0 \times 10^{-5}$ M, [Metal Nitrate] $= 0.01$ M.

compounds such as dithiols and can be applied widely to the synthesis of various cyclic polythioethers under mild conditions. The selectivity and yield of the reactions are relatively low, similar to previous methods,[30,31] but our method will be more advantageous than conventional methods for the preparation of cyclic polythioethers. Synthetic applications including the optimum reaction conditions now are being investigated in our laboratory.

EXPERIMENTAL

All reagents were commercially available chemicals. Melting points were determined on a Yanako Micro melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO FT/IR-300E spectrophotometer. Mass spectra were recorded on a HITACHI M-80B spectrometer. (EI) or a JEOL GCmate (FAB). NMR spectra were recorded on a JEOL GX-400.

1,1′-(Dithiobutane)diethaniminium Salt 3 ($R^1 = (CH_2)_4$): Typical Procedure

A mixture of thioacetamide, **1**, (15.03 g, 0.20 mmol) and 1,4-dibromobutane, **2** ($\mathbf{R}^1 = (\mathbf{CH}_2)_4$), (21.59 g, 0.10 mmol) in chloroform is refluxed for 2 h. After cooling, the precipitate is collected by filtration and washed with ether to give **3** ($\mathbf{R}^1 = (\mathbf{CH}_2)_4$) (34.31 g, 94%) as a colorless solid of m.p. 196–198°C. IR (KBr) cm^{-1}: 2850, 1620, 1269, 866, 694. HR-MS (FAB+) m/z: 285.0099 [$(M\text{-}Br)^+$] (Calcd for $C_8H_{18}N_2S_2Br$: 285.0094).

Cyclic Polythioethers 11: General Procedure

A mixture of the freshly prepared 1,1′-(dithioalkane) diethaniminium salt, **3**, (20 mmol), tetrabutyl-ammmonium bromide (TBAB; 0.64 g, 2.0 mmol) as phase-transfer catalyst, benzene (50 mL), and 30 wt% aqueous sodium hydroxide (100 g) is vigorously stirred at 60–65°C for 1 h under nitrogen atmosphere. The alkyl dibromide, **4**, (20 mmol) in benzene (50 mL) is then added dropwise to the solution over 4 h. The resulting solution is stirred further for 1 h. After the reaction, the organic layer is separated, and the aqueous layer is extracted with benzene. The combined organic layer is washed with water (3×100 mL), dried, and evaporated. The cyclic polythioethers include the 1:1 and 2:2 stoichiometric products (**5**) which are isolated from residual product by column chromatography on silica gel using hexane/EtOAc (9:1) as an eluent.

Solvent Extraction of Metal Ions[36]

An aqueous solution (3 mL) containing 1×10^{-2} M metal nitrate and 3×10^{-5} M picric acid was placed in a 10 mL glass cylindrical tube equipped with a glass stopper. After the addition of 3 mL of the 3×10^{-4} M cyclic polythioether (host) solution of 1,2-dichloroethane, the mixture was vigorously shaken for 30 min at 25°C. The concentration of the metal ion in the aqueous phase was determined by means of ultraviolet spectrophotometry.

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