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New Tin Templates for the Synthesis of Macrocyclic Polythiaether−Polythiaester Ligands

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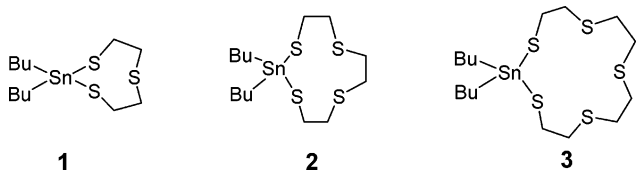
Abstract: The preparation of new tin templates, stannathianes **1**−**3** is described. New templates have been successfully applied to the synthesis of macrocyclic polythialactones **4**−**9** by cyclization of corresponding stannathianes **1**−**3** with pimeloyl dichloride.

The synthesis of macrocyclic polyethers from acyclic precursors has gained enormous importance over the years, especially by virtue of the development of supramolecular chemistry, in which macrocycles play a central role.[1]

Macrocyclic thiacrown ethers have been a subject of interest during the past three decades. Because of the softness of sulfur, these molecules are especially appropriate for complexation with heavy-metal ions such as Hg^{2+}, Ag^{+}, Cd^{2+}, and Pb^{2+}.[2]

Novel macrocycles are currently being developed and evaluated for use as selective recyclable ligands for extraction of heavy metals from contaminated waters.[3,4] Both acyclic sulfur-containing ligands and cyclic crown thiaethers have been used in such applications. The addition of an aliphatic cage structure to crown thiaethers has resulted in several macrocycles that are insoluble in protic solvents such as water and methanol.[5]

CHART 1



1 **2** **3**

The development of efficient and novel synthetic routes to new polythiamacrocycles is a worthy endeavor that will aid the design of a vast variety of new macrocyclic polythia compounds. Herein we present a new strategy that can be used to prepare macrocyclic polythia compounds via ring-opening condensation of new tin-containing polythiaethers. Cyclic stannapolythiane intermediates are employed as activated dithiols to promote efficient syntheses of macrocyclic polythiaether−ester ligands.

It is well-known that organotin compounds function effectively as transesterification catalysts and also serve as efficient initiators to promote ring-opening polymerization of lactones.[6] This method also has been applied for the preparation of macrocyclic di- and tetralactones.[7] Recently, an improved procedure for the synthesis of macrocyclic polythialactones by using stannathianes has been reported.[8] The demonstrated efficiency of this method encouraged us to employ a similar strategy to prepare several new tin templates (i.e. **1**−**3**, Chart 1) and to apply them as intermediates in the synthesis of di- and tetralactone containing polythiaether chains (i.e. **4**−**9**, Scheme 1).

Stannathiane **1** was prepared in good yield (83%) by treatment of dibutyltin oxide with dithiol **11**. The reaction performed under the same conditions with thiols **12** and **13** gave no condensation products. However, when *p*-TsOH was used as the catalyst, tin templates **2** and **3** were obtained in 50% and 60% yield, respectively, in addition to the lower homologues **1** and **2**.[9] A reasonable mechanism that accounts for the formation of the lower homologues via acid-catalyzed condensation is shown in Scheme 2. In addition to cyclization to afford stannathiane **2**, formation of thionium ion **14** also can occur. Subsequently, **14** is expected to decompose to produce stable stannathiane **1**.

It should be noted that stannathianes **2** and **3** are sensitive to degradation. All attempts to separate stan-

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(9) In the synthesis of stannathiane **2**, besides **2**, lower homologue tin template **1** was formed in 25% yield. In the synthesis of stannathiane **3**, besides **3**, lower homologues tin templates **2** and **1** were formed in 20% and 10% yield, respectively.

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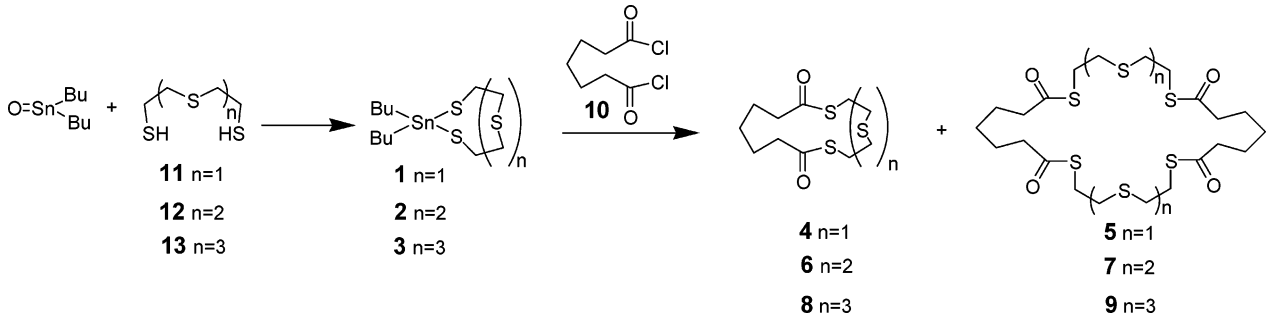
SCHEME 1



SCHEME 2

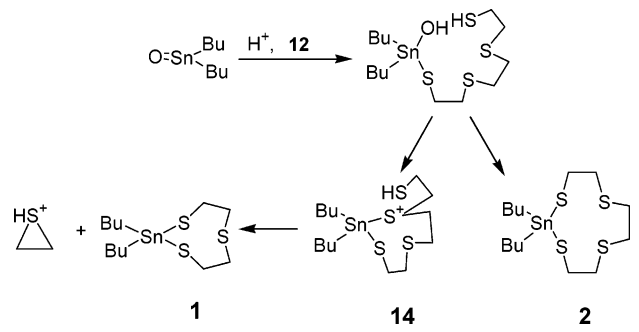


TABLE 1. Reaction of Acid-Dichloride 10 with Tin Template 1, 2, and 3

tin template	products	yield (%)[a]	Ms (*m/e*)[b]	(k'_n)[c]
1	**4**	62	278 (M^+)	0.10
	5	20	556 (M^+); 279 (M/2 + 1)	0.61
2	**6**	45	338 (M^+)	0.40
	7	9	676 (M^+); 339 (M/2 + 1)	1.11
3	**8**	28	398 (M^+)	0.42
	9	7	796 (M^+); 399(M/2 + 1)	1.18

[a] Isolated yield. [b] EI method. [c] HPLC capacity factor of the eluted compound ($k'_n = t_n - t_0/t_0$).

nathiane **2** from **1** or **3** from **2** and **1** with chromatography on silica gel resulted in decomposition to starting dithiols. However, separation of stannathiane **1** from **2** could be carried out via careful fractional crystallization in pentane (see the Experimental Section).

The experiments carried out with pimeloyl dichloride (**10**) proved that the tin templates **1**, **2**, and **3** could be used efficiently to prepare macrocyclic polythia lactones **4**−**9**, as indicated in Scheme 1. Macrocyclic cyclization was achieved by slow addition of pimeloyl dichloride (**10**) into a refluxing solution of the appropriate tin-containing template. The yields of thialactones **4**−**9** ranged from 7% to 62% (Table 1).

All new compounds were characterized by analysis of their respective IR, proton NMR, and carbon-13 NMR spectra (see the Experimental Section) and by elemental microanalysis and/or HRMS. Mass spectral data and HPLC retention time were employed to distinguish the monomers **4**, **6**, and **8** from the dimers **5**, **7**, and **9**. Mass spectra of **4**, **6**, and **8** showed molecular ion peaks whereas the corresponding mass spectra of dimers **5**, **7**, and **9** display intense molecular ion and also (M/2 + 1) ion signals.

In summary, we have prepared hitherto unknown tin templates **1**−**3**. These compounds are very useful building blocks for making compounds such as macrocyclic polythialactones **4**−**9**, as well as a variety of compounds that could be used for soft metal complexation. Other applications of the new tin templates **1**−**3** are under investigation.

Experimental Section

Instruments and Materials. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on 300- and 600-MHz spectrometers. HPLC analyses were performed on an instrument equipped with a UV detector operated at λ 230 nm. An OmniSpher C18 (250 × 4.6 mm^2) chromatography column was employed by eluting with CH_3CN at a flow rate of 1 mL/min. Dibutyltin oxide and 2,2′-thiadiethanolthiol **11** were used as obtained from commercial sources. 3,6-Dithiaoctane-1,8-dithiol (**12**) was prepared according to the literature procedure.[10] Unless stated otherwise, reagent grade solvents were used.

Synthesis of 2,2-Dibutyl-2-stanna-1,3,6-trithiacyclooctane (1). In a two-necked flask fitted with a Dean−Stark apparatus was placed dibutyltin oxide (5.0 g, 20 mmol) and toluene (100 mL), and the resulting suspension was heated to reflux. Subsequently, a solution of 2,2′-thiadiethanthiole (2.9 mL; 20 mmol) in toluene (25 mL) was added dropwise with stirring to the refluxing reaction mixture during 5 h. After the addition of reagent had been completed, the resulting mixture was refluxed for 24 h, cooled to ambient temperature, and then concentrated in vacuo. The residue (8.2 g) was purified via column chromatography on silica gel by using a 0→50% EtOAc−hexane gradient elution scheme. Workup of the eluent thereby obtained afforded pure **1** (6.4 g, 83%) as a colorless oil. IR (KBr) 2955, 2918, 2872, 2851, 1462, 1421, 1268, 1195, 697 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.92 (6H, t, CH_3), 1.33−1.47 (8H, m), 1.62−1.69 (4H, m), 2.77−2.82 (4H, m), 2.92−2.96 (4H, m); ^{13}C NMR (600 MHz, $CDCl_3$) δ 13.5, 21.5, 26.6, 27.2, 28.1, 39.4. Anal. Calcd for $C_{12}H_{26}S_3Sn$: C, 37.41; H, 6.80. Found: C, 37.03; H, 6.53.

Synthesis of 2,2-Dibutyl-2-stanna-1,3,6,9-tetrathiacycloundecane (2). In a two-necked flask fitted with a Dean−Stark apparatus was placed toluene (80 mL) and a catalytic amount of *p*-TsOH, and the resulting mixture was heated to reflux. Then, a mixture of dibutyltin oxide (1.2 g, 5 mmol) and 3,6-dithiaoctane-1,3-dithiol (**12**, 1.1 g, 5 mmol) was added portionwise to the refluxing reaction mixture with stirring for 4 h. After the addition of reagents had been completed, the resulting mixture was refluxed overnight, then cooled to ambient temperature and concentrated in vacuo. The residue was filtered through a small pad of silica to remove *p*-TsOH, which subsequently was rinsed with 50% EtOAc−hexane. The filtrate was concentrated, thereby affording a mixture (1.7 g) of two products, i.e., tin templates **2** and **1** (product ratio 2:1, respectively). Product **1** could be removed from the mixture by fractional crystallization from pentane. IR (KBr) 2960, 2934, 2873, 2854, 1464, 1425, 1263, 1197, 695 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (6H, t, CH_3), 1.30−1.70 (12H, m), 2.75−3.25 (12H, m); ^{13}C NMR (300 MHz, $CDCl_3$) δ 13.4, 18.4, 26.6, 27.6, 28.1, 32.5, 35.9.

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Synthesis of 2,2-Dibutyl-2-stanna-1,3,6,9,12-pentathiacyclotetradecane (3). In a two-necked flask fitted with a Dean−Stark apparatus was placed toluene (80 mL) and a catalytic amount of *p*-TsOH, and the resulting mixture was heated to reflux. Then, a mixture of dibutyltin oxide (1.0 g, 4 mmol) and 3,6,9-trithiaundecane-1,3-dithiol (**13**, 1.1 g, 4 mmol) was added portionwise to the refluxing reaction mixture with stirring for 4 h. After the addition of reagents had been completed, the resulting mixture was refluxed overnight, at which time the reaction mixture was allowed to cool to ambient temperature and then concentrated in vacuo. The residue was filtered through a small pad of silica and rinsed with 50% EtOAc−hexane. The filtrate was concentrated, thereby affording a mixture (1.8 g) of three products, i.e., tin templates **3**, **2**, and **1**. According to the ^{13}C NMR spectra the product ratio of **3**, **2**, and **1** was 6:2:1, respectively. Since tin templates **2** and **3** are decomposing on silica gel, the obtained product mixture was used in the next step without further purification. **3**: ^1H NMR (600 MHz, $CDCl_3$) δ 0.93 (6H, t, CH_3), 1.33−1.43 (4H, m), 1.44−1.51 (4H, m), 1.62−1.68 (4H, m), 2.79−2.85 (12H, m), 2.92−2.96 (4H, m); ^{13}C NMR (600 MHz, $CDCl_3$) δ 13.4, 18.3, 26.59, 27.62, 28.1, 31.4, 32.2, 35.2.

Preparation of Macrocyclic Thiaesters: General Procedure. A solution of stannathiane **1**, **2**, or **3** (1 mmol) in dry $CHCl_3$ (30 mL) was heated to reflux, and a solution of 1,7-heptandioyl dichloride (**10**) (1 mmol) in dry $CHCl_3$ (10 mL) was added dropwise to the reaction mixture with stirring for 1 h. After the addition of reagents had been completed, the resulting mixture was refluxed overnight, at which time the reaction mixture was allowed to cool to ambient temperature and then treated with 2,2′-bipyridyl (1 mmol). The resulting mixture was filtered through a small pad of silica, and the filtrate was concentrated in vacuo. A gross mixture of products was thereby obtained as a thick, colorless oil.

Monomeric Trithiaester 4 and Dimeric Hexathiaester 5. By following the general procedure described above, compounds **4** and **5** were obtained via reaction of stannathiane **1** (390 mg, 1 mmol) with the appropriate diacyl dichloride **10** (197 mg, 1 mmol). The crude reaction product was purified by column chromatography on silica gel by using a 0→20% of EtOAc−CH_2Cl_2 gradient elution scheme. In this way, pure trithiaester **4** (173 mg, 62%) and hexathiaester **5** (56 mg, 20%) were obtained as white crystalline solids.

2,5,8-Trithiacyclotetradecane-1,9-dione (4): mp 118−119 °C; IR (KBr) 2925, 2857, 1679, 1431, 1260, 1100, 1036, 948 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.38−1.48 (2H, m), 1.64−1.72 (4H, m), 2.48−2.55 (4H, m), 2.75−2.81 (4H, m), 3.08−3.13 (4H, m); ^{13}C NMR (600 MHz, $CDCl_3$) δ 25.5, 26.0, 28.6, 33.1, 43.0, 198.9; HRMS for $C_{11}H_{18}O_2S_3$ (M^+) calcd 278.046347, found 278.043494. Anal. Calcd for $C_{11}H_{18}O_2S_3$: C, 47.45; H, 6.52. Found: C, 47.26; H, 6.43.

2,5,8,16,19,22-Hexathiacyclooctacosane-1,9,15,23-tetraone (5): mp 98−100 °C; IR (KBr) 2935, 2852, 1685, 1467, 1423, 1102, 1017, 969 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.34−1.44 (4H, m), 1.65−1.73 (8H, m), 2.55−2.62 (8H, m), 2.74−2.81 (8H, m), 3.07−3.14 (8H, m); ^{13}C NMR (600 MHz, $CDCl_3$) δ 25.03, 27.80, 29.09, 31.94, 43.55, 198.54; HRMS for $C_{22}H_{36}O_4S_6$ ($M + H)^+$ calcd 557.101068, found 557.101752. Anal. Calcd for $C_{22}H_{36}O_4S_6$: C, 47.45; H, 6.52. Found: C, 47.14; H, 6.54.

Monomeric Tetrathiaester 6 and Dimeric Octathiaester 7. By following the general procedure described above, compounds **6** and **7** were obtained via reaction of stannathiane **2** (890 mg, 2 mmol of the mixture of stannathianes **1** and **2** in a ratio of 1:2, respectively) with the appropriate diacyl dichloride **10** (390 mg, 2 mmol). The crude reaction product was purified by column chromatography on silica gel by using a 0→20% of EtOAc−CH_2Cl_2 gradient elution scheme. In this way, pure tetrathiaester **6** (190 mg, 45% regarding the stannathiane **2**) was obtained as a colorless oil, followed by trithiaester **4** (64 mg) and octathiaester **7**[11] (38 mg, 9% regarding the stannathiane **2**) as a colorless wax.

2,5,8,11-Tetrathiacycloheptadecane-1,12-dione (6): IR (KBr) 2930, 2863, 1692, 1422 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.31−1.40 (2H, m), 1.59−1.69 (4H, m), 2.52−2.54 (4H, m), 2.64−2.70 (4H, m), 2.81 (4H, br s), 2.96−3.01 (4H, m); ^{13}C NMR (600 MHz, $CDCl_3$) δ 24.5, 26.3, 29.0, 32.2, 32.8, 42.8, 198.6; HRMS for $C_{13}H_{22}O_2S_4$ (M^+) calcd 338.0472, found 338.0503. Anal. Calcd for $C_{13}H_{22}O_2S_4$: C, 46.12; H, 6.55. Found: C, 46.32; H, 6.56.

2,5,8,11,19,22,25,28-Octathiacyclotetratriacontane-1,12,-18,29-tetraone (7): IR (KBr) 2935, 2860, 1685, 1465, 1420, 1190, 1030 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.1.33−1.43 (4H, m), 1.62−1.75 (8H, m), 2.55−2.64 (8H, m), 2.66−2.90 (16H, m), 3.05−3.13 (8H, m); ^{13}C NMR (600 MHz, $CDCl_3$) δ 25.0, 28.0, 29.0, 31.6, 31.8, 43.6, 198.6; HRMS for $C_{26}H_{44}O_4S_8$ ($M + H)^+$ calcd 677.107812, found 677.107922.

Monomeric Pentathiaester 8 and Dimeric Decathiaester 9. By following the general procedure described above, compounds **8** and **9** were obtained via reaction of stannathiane **3** (1.0 g, ca. 2 mmol of the mixture of stannathianes **1**, **2**, and **3** in a ratio of 1:2:6, respectively) with the appropriate diacyl dichloride **10** (390 mg, 2 mmol). The crude product was purified by column chromatography on silica gel by using a 0→20% of EtOAc−CH_2Cl_2 gradient elution scheme. In this way, tetrathiaester **6** (70 mg), pure pentathiaester **8** (206 mg, 28% regarding the stannathiane **3**), and trithiaester **4** (20 mg) were obtained as colorless oils, and decathiaester **9**[11] (50 mg, 7% regarding the stannathiane **3**) was obtained as a colorless wax.

2,5,8,11,14-Pentathiacycloicosane-1,15-dione (8): IR (KBr) 2929, 2862, 1693, 1424 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.29−1.42 (2H, m), 1.55−1.68 (4H, m), 2.48−2.56 (4H, m), 2.60−2.68 (4H, m), 2.82 (8H, br s), 2.93−3.03 (4H, m); ^{13}C NMR (300 MHz, $CDCl_3$) δ 24.8, 27.6, 28.7, 31.4, 31.8, 32.0, 43.5, 198.6; HRMS for $C_{13}H_{22}O_2S_a$ (M^+) calcd 398.053091, found 398.049580. Anal. Calcd for $C_{15}H_{26}O_2S_5$: C, 45.19; H, 6.57. Found: C, 44.82; H, 6.89.

2,5,8,11,14,22,25,28,31,34-Decathiacyclotetracontane-1,-15,21,35-tetraone (9): IR (KBr) 2925, 2853, 1683, 1425, 1190, 1044 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.32−1.43 (4H, m), 1.60−1.73 (8H, m), 2.52−2.61 (8H, m), 2.66−2.86 (24H, m), 3.02−3.12 (8H, m); ^{13}C NMR (300 MHz, $CDCl_3$) δ 25.0, 28.0, 28.9, 31.8, 32.0, 32.1, 43.6, 198.6; HRMS for $C_{30}H_{52}O_4S_{10}$ ($M + H)^+$ calcd 797.114556, found 797.114675.

Preparation of 3,6,9-Trithiaundecane-1,11-dithiol (13). A solution of thiourea (608 mg, 8.0 mmol) in 95% aqueous EtOH (15 mL) was heated gently at 40 °C. To the warm reaction mixture was added dropwise with stirring 3,6,9-trithiaundecane-1,11-dichloride[12] (968 mg, 4.0 mmol). The initial suspension dissolved upon heating to form a clear solution. The resulting mixture was refluxed for 2 h and then was allowed to cool gradually to ambient temperature. The cooled reaction mixture was concentrated in vacuo, and the oily residue was treated with a solution of KOH (3.6 g, 60 mmol) in water (30 mL). The resulting mixture was refluxed with stirring for 40 min and then allowed to cool gradually to ambient temperature. The resulting suspension was acidified with concentrated HCl (to pH 3) and extracted with CH_2Cl_2 (2 × 40 mL). The organic extract was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. Pure **13** (760 mg, 69%) was thereby obtained as a colorless microcrystalline solid. Mp 64−67 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 1.74−1.77 (2H, t), 2.71−2.83 (16H, m); ^{13}C NMR (600 MHz, $CDCl_3$) δ 24.6, 32.1, 32.3, 36.2. Anal. Calcd for $C_8H_{18}S_5$: C, 33.73; H, 6.60. Found: C, 33.96; H, 6.67.

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(11) The cyclic dimers **7** and **9** were contaminated by minor amounts of polymeric material and **4**, as shown by HPLC and ^{13}C NMR.

(12) 3,6,9-Trithiaundecane-1,11-dichloride was prepared by reacting 3,6,9-trithiaundecane-1,11-diol[13] with thionyl chloride at room temperature. It should be noted that 3,6,9-trithiaundecane-1,11-dichloride is highly toxic and should be converted as soon as possible to the thiole **13**. Also all safety precausions should be taken.

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Supporting Information Available: NMR spectroscopic data including ^{1}H and ^{13}C NMR spectra for compounds **1**, **2**, **4**−**6**, and **8**, as well as ^{13}C NMR spectra for compounds **7** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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