AD-A133 697 MACROCYCLES CONTAINING TIN SYNTHESES OF SYMMETRICAL MACROCYCLES CONTAININ.. (U) TEXAS A AND M UNIV COLLEGE STATION DEPT OF CHEMISTRY M NEWCOMB ET AL. 07 OCT 83 1/1

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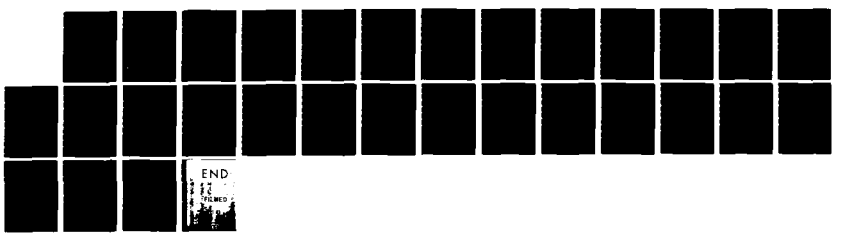

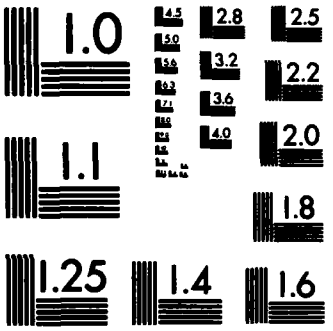

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The syntheses of macrocycles containing two diphenylstanna moieties, cyclo-$(Ph_2Sn(CH_2)_n)_2$ (1, n = 4, 5, 6, 8, 10, 12), and four diphenylstanna moieties, cyclo-$(Ph_2Sn(CH_2)_n)_4$ (2, same n), are reported. α,ω-bis(Bromomagnesio)alkanes reacted with Ph_3SnCl to give α,ω-bis(triphenylstannyl)alkanes which upon treatment with HBr gave α,ω-bis(bromodiphenylstannyl)alkanes (4). Compounds 4 reacted with the corresponding chain length α,ω-bis(bromomagnesio)alkanes

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to give 1 and 2. Alternatively, good yields of 1 (n = 4, 5, 6, 8) were obtained by converting 4 to dilithium reagents (7) which were allowed to react with α,ω-dibromoalkanes. Good yields of 2 (n = 4, 5, 6) were obtained by first treating 4 with $Cl(CH_2)_nMgBr$ to give dichlorides which were then allowed to react with 7 in a second step. Purifications of the macrocycles and several synthetic intermediates were effected by preparative reverse phase chromatography. The macrocyclic products were characterized by NMR spectroscopy, molecular weight determinations and elemental analyses.

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TECHNICAL REPORT NO. 4

Macrocycles Containing Tin.

Syntheses of Symmetrical Macrocycles Containing Two or Four Diphenylstanna Units

by

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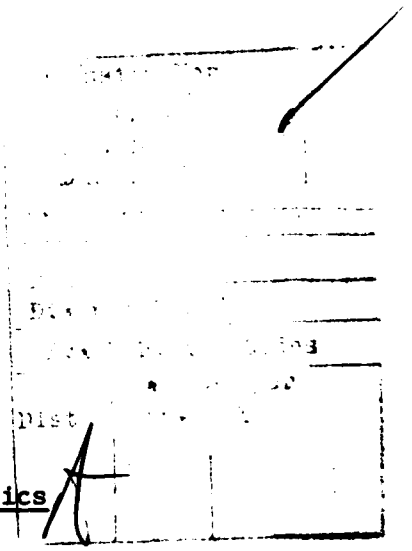

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Abstract: The syntheses of macrocycles containing two diphenylstanna moieties, cyclo-[$Ph_2Sn(CH_2)_n$-]$_2$ (1, n = 4, 5, 6, 8, 10, 12), and four diphenylstanna moieties, cyclo-[$Ph_2Sn(CH_2)_n$-]$_4$ (2, same n), are reported. α,ω-bis(Bromomagnesio)alkanes reacted with Ph_3SnCl to give α,ω-bis(triphenylstannyl)alkanes which upon treatment with HBr gave α,ω-bis(bromodiphenylstannyl)alkanes (4). Compounds 4 reacted with the corresponding chain length α,ω-bis(bromomagnesio)alkanes to give 1 and 2. Alternatively, good yields of 1 (n = 4, 5, 6, 8) were obtained by converting 4 to dilithium reagents (7) which were allowed to react with α,ω-dibromoalkanes. Good yields of 2 (n = 4, 5, 6) were obtained by first treating 4 with $Cl(CH_2)_nMgBr$ to give dichlorides which were then allowed to react with 7 in a second step. Purifications of the macrocycles and several synthetic intermediates were effected by preparative reverse phase chromatography. The macrocyclic products were characterized by NMR spectroscopy, molecular weight determinations and elemental analyses.

Macrocyclic and macrobicyclic compounds containing the basic atoms oxygen, nitrogen and sulfur have been widely exploited in cation coordination chemistry during the past decade. In various applications including solublization of salts in organic media, chromatographic separations and catalysis, the dominant features of this chemistry are the size of the cavities formed by the basic atoms of the host compounds and the fit of cationic guests within these cavities. Little work has been reported concerning macrocycles containing Lewis acidic atoms which might show selective complexing behavior as anion coordination agents or in binding to neutral donor compounds even though such compounds should also enjoy a rich chemistry. In accord with this expectation, polyammonium macrocycles have recently been shown to exhibit selective behavior in binding to anions and basic donors.[2] The use of protonated or alkylated amine-containing macrocycles or macrobicycles as anion coordinating agents, however, may show limitations with the range of solvents which can be employed.

We reasoned that macrocyclic compounds containing tin atoms as Lewis acidic sites could function as anion or basic neutral coordinating species and show good solubility in organic solvents. Complexation of tin-containing compounds which contain electron-withdrawing groups on the tin atoms with basic donors has been widely observed, and organostannate(IV) complexes are known.[3] Recently, Kuivila's and Gielen's groups have reported complexes of donors with compounds containing two Lewis acidic tin atoms.[4,5] Since limited examples of organometallic compounds containing more than one tin atom have been reported, we have established general procedures for the synthesis of a wide range of macrocycles containing tin atoms. In this paper we describe three

related procedures for the syntheses of symmetrical macrocycles containing two diphenylstannyl moieties (1, ring size 10 to 26) or four diphenylstannyl moieties (2, ring size 20 to 52).[6,7] Our synthetic and purification procedures have permitted the isolation of tin-containing macrocycles in gram batches.

Results and Discussion

Scheme I shows the pathways which we have employed for the synthesis of tin-containing macrocycles 1 and 2. The starting materials for each route are the α,ω-bis(triphenylstannyl)alkanes (3) obtained from the reaction of an α,ω-bis(bromomagnesio)alkane with Ph_3SnCl. For carbon chain lengths ranging from 4 to 12, the isolated yields of compounds 3 were 68 to 80%. Compound 3a had been prepared previously in low yield by a similar route.[11] The synthesis of 1,3-bis(metallo)propanes via the diGrignard route requires a circuitous preparation of 1,3-bis(bromomagnesio)propane[12] which we chose not to employ, however, 1,3-bis(triphenylstannyl)propane has been prepared,[5] and 1,3-bis(trimethylstannyl)propane is available from the reaction of trimethylstannyllithium with 1,3-dibromopropane.[13]

(INSERT SCHEME 1)

The conversion of the α,ω-bis(triphenylstannyl)alkanes to their corresponding α,ω-bis(bromodiphenylstannyl)alkanes (4) proved to be more difficult than we had expected. Bromine in CCl_4 or pyridine or phenyltrimethylammonium perbromide reacted with compound 3a to give mixtures of products which were difficult to purify. NMR spectroscopic studies of these mixtures suggested that a second phenyl group was cleaved from tin almost as readily as the first leading to mono-, di- and tri-bromination

of 3a.[14,15] However, when compounds 3 were treated with 2.1 equivalents of HBr in CH_2Cl_2 at -78 °C and the resulting mixtures were allowed to warm to room temperature slowly, we obtained good yields of the desired dibromides 4. Most of these products were oils which were purified by reverse phase chromatography as described below.

There are alternative methods for the functionalization of compounds 3. Zimmer has reported the conversion of 3a to 1,4-bis(iododiphenylstannyl)butane,[16] and α,ω-bis(chlorodiphenylstannyl)-propane and -butane have been reported.[5]

Our ability to obtain compounds 4 in good yield permitted the synthesis of tin-containing macrocycles by the various routes shown in Scheme 1. In the first procedure, Method A, an α,ω-bis(bromomagnesio)-alkane (6) was prepared in tetrahydrofuran (THF). After titration of an aliquot, the solution of the diGrignard reagent was diluted to 0.02-0.03 M, and the resulting solution was added over 2 h to a ca. 0.03 M THF solution of the corresponding chain length bis(bromodiphenylstannyl)-alkane. With these reasonably dilute solutions, the macrocyclizations to give 1 and 2 were possible.

Macrocycles 1 and 2 were isolated from the crude product mixtures by preparative reverse phase chromatography. Although analytical HPLC could be effected with methanol or ethanol/water elution, mixtures of THF in acetonitrile were used in the preparative LC in order to permit dissolution of the product mixtures in 0.2-0.5 gram batches. In all cases the bis(diphenylstanna)cycloalkanes (1) eluted before their tetrakis-(diphenylstanna) analogues (2) of twice the molecular weight; typically the α value for separation of 1 and 2 was about 3, and resolution of these products was not difficult. Other low yield products, presumably open-chain species with molecular weights similar to 1 and 2, eluted with

retention times similar to the desired cyclic products. Most of the macrocyclic products were readily recrystallized after chromatographic purification.

Method A is a "shotgun" procedure which gives rise to macrocycles 1 in a two-component cyclization and macrocycles 2 in a four-component cyclization. Polymerization of the growing chains competes with cyclization, and high weight compounds appear to be the major by-products in the product mixtures. The cyclizations giving rise to the smaller rings 1a and 1b apparently suffer some steric strain and the yields of the these compounds are slightly lower than those of the larger ring compounds 1c-1f (Figure 1, Table 1) even though the effective molarity of one chain end for the other end of the chain could be relatively high. At carbon chain lengths of 6 atoms or more the yield of the bis(diphenylstannyl)-cycloalkanes 1 are relatively constant. The yields of the tetrakis-(diphenylstanna)cycloalkanes (2), however, dropped off rapidly when the linking chain reached a length of 6 carbon atoms (Figure 1). In these cases the penultimate intermediate before cyclization to 2 was a long acycle ()28 atoms), and the effective molarity for the chain ends apparently had fallen below the actual molarity of the reagents. This behavior is in accord with that seen in other macrocyclization reactions.[17]

(INSERT TABLE 1)

(INSERT FIGURE 1)

Macrocycles were also formed (in another "shotgun" reaction) when the α,ω-bis(bromodiphenylstannyl)alkanes 4 were first converted to their corresponding dilithium reagents (7) in a reaction with lithium metal, and then dilute THF solutions of reagents 7 were added to dilute THF

solutions of α,ω-dibromoalkanes 5 (Method B). In this method, the role of the nucleophile and the electrophile in the coupling reaction have been reversed. The concentrations of the reagents, addition times and reaction temperatures were comparable to those used in Method A and the nucleophilic reagents were again added to the electrophilic species, however, the yields of macrocyclic products were substantially different than those obtained in Method A (Table 1). Specifically, we found that the bis(diphenylstanna)cycloalkanes 1a-d were formed in good yields, but only traces (<2%) of the corresponding tetrakis(diphenylstanna) analogues were produced.

The dramatic changes in yields of 1 and 2 produced in Method B relative to those in Method A cannot be attributed to the efficiency of formation of the nucleophilic reagents. In fact, the nucleophilic species were formed in lower yields in Method B; typically the total base was 90% in the preparation of reagents 6 and only 75% in the preparation of reagents 7. The high yields of 1 in Method B are consistent with relatively slow reactions of the bis(stannyllithium) compounds 7 with the α,ω-dibromides since higher yields of 1 would be expected if bulk mixing competes with the coupling reaction. However, our lack of knowledge concerning the structure, aggregation or reactivity of species 7 makes further speculation fruitless.[18]

Methods A and B can be seen to be of limited utility in the synthesis of the larger tetrakis(diphenylstanna)cycloalkanes 2. Thus, we developed a procedure in which compounds 2 are produced in a two- rather than a four-component macrocyclization (Method C). Treatment of the α,ω-bis(bromodiphenylstannyl)alkanes 4a-c with an excess of an α-(bromomagnesio)-ω-chloroalkane (formed in the reaction of an α-bromo-ω-chloroalkane with only one gram-atom equivalent of magnesium) afforded the open

chain α,ω-dichloro compounds 8a-c as colorless oils which were purified by reverse phase chromatography. Subsequently, the bis(diphenylstannyllithium) reagents 7 at high dilution were added to dilute solutions of dichlorides 8. After reverse phase chromatography and recrystallization, the isolated yields of tetrakis(diphenylstanna) macrocycles 2a-c obtained by this procedure were about 35% (Table 1). The 33% isolated yield of 2c obtained by Method C is an order of magnitude higher than the yield of 2c obtained from Method A.

Macrocycles 1 and 2 were characterized by NMR spectroscopy and osmometric molecular weight determinations. Acceptable elemental analyses for all of the macrocycles were obtained. ^{1}H NMR spectra of the isolated products clearly indicated the gross structure of the macrocycles; the molecular weight measurements permitted the complete structure assignment. Because of the symmetry of the macrocycles, quite simple ^{13}C NMR spectra were obtained.[20] The purities of the products were apparent from HPLC as well as from the sharp melting points, where applicable, and elemental analyses.

Elemental analyses were also obtained for the α,ω-bis(triphenylstannyl)-alkanes (3). Despite the fact that we purified the α,ω-bis(bromodiphenylstannyl)alkanes (4) and compounds 8, we considered these species to be reactive intermediates and did not attempt to store them for extended periods nor did we attempt to obtain elemental analyses or molecular weights of these compounds which, with the exception of 4a, were oils. The identities of compounds 4 and 8 are established by their NMR spectra and the successful synthesis of the fully characterized macrocycles from these intermediates.

The use of preparative reverse phase chromatography for the isolation of macrocycles deserves comment. Even though most of the macro-

cyclic compounds we prepared were crystalline, no products of the macrocyclization reactions were obtained pure without chromatography. The preparative phase we used was highly reproducible, retention times in preparative chromatography were easily predicted by inspection of the analytical HPLC chromatogram, and excellent peak shapes were maintained at loading ratios as high as 1 gram of crude reaction mixture on 300 grams of support. Further, the high initial costs of the preparative phase were offset by the fact that after ca 50 preparative runs we saw no change in the capacity or retention characteristics of our preparative columns.

We have briefly studied some reactions of macrocycles and models in order to determine what reagents would be appropriate for both the synthesis and subsequent functionalization of these compounds. Triphenylbutyltin was found to react rapidly with an excess of n-BuLi in THF even at -78 °C. Thus the reaction of an α,ω-dilithioalkane with a bis(bromodiphenylstannyl)alkane would not be expected to give macrocycles in good yield, especially if the dibromo compound was added to the dilithioalkane, but macrocycles containing less reactive alkyl groups on the tin may survive such reaction conditions. When macrocycles 1a and 2a were treated with 2.1 and 4.2 equivalents of HBr in CH_2Cl_2, respectively, in a procedure similar to the bromination of acycles 3, ^{1}H NMR spectra of the crude reaction products indicated good conversion to derivatives containing (bromophenylstanna) moieties with no evidence of ring cleavage. This functionalization of the macrocycles is a critical step required to impart Lewis acid character to the tin atoms in order to permit their application as anion or neutral donor coordinating hosts. The details of these continuing studies will be reported in due course.

The procedures described above afford the bis(diphenylstanna)- (1)

and tetrakis(diphenylstanna)cycloalkanes (2) in fair to good yields. Macrocycles with ring sizes from 10 to 52 atoms have been prepared.[21] It may be expected that higher yields of the macrocycles could be obtained if an apparatus which delivered dilute solutions of both reactive precursors to a reaction vessel were employed, but by the methods described herein we have isolated up to gram quantities of several of the desired macrocycles.

Experimental Section

General. All reactions of organolithium and Grignard reagents were run in a nitrogen atmosphere; transfers were made by syringe or cannula. Commercial organic halides (Aldrich) were distilled before use. Triphenyltin chloride (Alfa) was used without further purification. Tetrahydrofuran (THF) was distilled from potassium-benzophenone immediately before use. "Brine" refers to a saturated aqueous sodium chloride solution. Yields of organolithium reagents and Grignard reagents used in the syntheses were determined by titration of a one mL aliquot of these solutions for active base before addition of these solutions to the appropriate electrophile[23] The endpoints were readily apparent in the titrations of the Grignard reagents. However, because of the color of the stannyllithium reagents, endpoints in these titrations were difficult to observe, and the total yield of nucleophilic reagents found in Methods B and C below must be considered to be approximate.

^{1}H NMR spectra of $CDCl_3$ solutions were recorded on a Varian EM 390 spectrometer, and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded on a JEOL PFT-100 spectrometer; chemical shifts are reported in ppm downfield from internal Me_4Si. IR spectra were recorded on a Sargent-Welch 3-200 IR spectrophotometer. Molecular weights were measured on $CHCl_3$ solutions using a Hewlett-Packard model 302 B vapor pressure osmometer; periodic molecular weight measurements of standard solutions of benzil showed <5% error. In most of the molecular weight determinations, the concentration of only one solution of the substrate was determined. HPLC analyses were performed on 25 cm columns containing Spherisorb ODS-10, and preparative LC separations were accomplished on reverse phase C-18 bonded to silica gel (40 μ) supplied by J. T Baker, Co.; UV detection at 254 nm was used in both cases. The preparative LC system was composed of a low pressure solvent pump, a

(Greek "mu")

standard six-way plastic valve for injection, commerical glass columns (Ace), and an ISCO detector. Analyses were performed at Texas A&M University or at Galbraith Laboratories, Inc., Knoxville, Tennessee.

Preparation of α,ω-bis(triphenylstannyl)alkanes (3). To a suspension of 10 equiv of Mg and a small crystal of I_2 in THF was added a solution of α,ω-dibromoalkane in THF (0.3-0.4 M) over 1.5-2 h at 25 °C with stirring. After 5-8 h, a one mL aliquot was titrated for active base; yields from the dibromide were 75-90%. The α,ω-bis(bromomagnesio)alkane[24] solution was separated from excess Mg by cannula transfer and added to a solution of 2 equiv of Ph_3SnCl in THF (1.0-1.5 M) over 2 h at 0 °C. The reaction mixture was allowed to warm to 25 °C, and the reaction mixture was stirred for 8-10 h and then heated at reflux for 2 h. The reaction was quenched by the addition of 50-70 mL of satd aq NH_4Cl solution at 0 °C. The organic layer was separated, and the aqueous layer was extracted with ether (3 x 50 mL). The combined organic solutions were washed with a satd aq KF solution (50 mL) and brine, and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo*, and the residue was purified by recrystallization or column chromatography. The reactions were run on a scale to give a 30-40 g isolated yield of compounds **3**.

1,4-bis(Triphenylstannyl)butane (**3a**), purified by recrystallization from a mixture of CH_2Cl_2 and hexane (1:2, v:v), was obtained in 78% yield: mp 148.5-149 °C (lit.[11] mp 149-150.5 °C). IR (Nujol): 1070 cm^{-1}. ^1H NMR: 1.30-1.60 (4 H, m), 1.65-1.90 (4 H, m), 7.10-7.53 (30 H, m). ^{13}C NMR: 138.9, 137.0, 128.7, 128.4, 31.3, 10.6. MW: 734 (calcd for $C_{40}H_{38}Sn_2$, 755). Anal. Calcd for $C_{40}H_{38}Sn_2$: C, 63.54; H, 5.07. Found: C, 63.59; H, 5.22.

1,5-bis(Triphenylstannyl)pentane (**3b**), purified by recrystallization from hexane or a mixture of CH_2Cl_2 and hexane (1:3, v:v), was obtained in

80% yield: mp 72-73 °C. IR (Nujol): 1072 cm^{-1}. ^1H NMR: 1.20-1.83 (10 H, m), 7.13-7.50 (30 H, m). MW: 745 (calcd for $C_{41}H_{40}Sn_2$, 769). Anal. Calcd for $C_{41}H_{40}Sn_2$: C, 63.94; H, 5.24. Found: C, ~~64.14~~; H, ~~5.27~~ 5.17.

1,6-bis(Triphenylstannyl)hexane (3c), purified by recrystallization from hexane, was obtained in 68% yield: mp 84-85 °C. IR (Nujol): 1070 cm^{-1}. ^1H NMR: 1.2-1.83 (12 H, m), 7.20-7.83 (30H, m). MW: 770 (calcd for $C_{42}H_{42}Sn_2$, 783). Anal. Calcd for $C_{42}H_{42}Sn_2$: C, 64.33; H, 5.40. Found: C, 64.43; H, 5.52.

1,8-bis(Triphenylstannyl)octane (3d), purified by recrystallization from a mixture of hexane-ether (2:1, v:v), was obtained in 70% yield: mp 101-104 °C. IR (Nujol): 1070 cm^{-1}. ^1H NMR: 1.00-1.80 (16 H, m), 7.13-7.67 (30 H, m). MW: 808 (calcd for $C_{44}H_{46}Sn_2$, 811). Anal. Calcd for $C_{44}H_{46}Sn_2$: C, 65.06; H, 5.71. Found: C, 65.19; H, 5.81.

1,10-bis(Triphenylstannyl)decane (3e), purified by recrystallization from hexane, was obtained in 76% yield: mp 45-46 °C. IR (Nujol): 1074 cm^{-1}. ^1H NMR: 1.00-1.90 (20 H, m), 7.20-7.63 (30 H, m). MW: 836 (calcd for $C_{46}H_{50}Sn_2$, 839). Anal. Calcd for $C_{46}H_{50}Sn_2$: C, 65.75; H, 6.00. Found: C, 65.88; H, 6.08.

1,12-bis(Triphenylstannyl)dodecane (3f), purified by column chromatography on silica gel with hexane elution, was obtained in 70% yield: mp 41-43 °C or oil. IR (Nujol): 1070 cm^{-1}. ^1H NMR: 1.07-1.88 (24 H, m), 7.23-7.63 (30 H, m). MW: 865 (calcd for $C_{48}H_{54}Sn_2$, 867). Anal. Calcd for $C_{48}H_{54}Sn_2$: C, 66.39; H, 6.27. Found: C, 66.57; H, 6.19

Preparation of α,ω-bis(bromodiphenylstannyl)alkanes (4). To a solution of 3 in CH_2Cl_2 (0.1-0.2 M) was slowly (2 h) added a solution of 2.1 equiv of HBr in CH_2Cl_2 (0.2-0.3 N) at -78 °C. The reaction mixture was slowly allowed to warm to 25 °C. After 8-10 h, the solvent was removed in vacuo to give a crude product. Compounds 4b-f were isolated by reverse phase column

chromatography (C-18) by elution with dry CH_3CN or a mixture of CH_3CN and THF. Compound 4a was purified by recrystallization. Compounds 4 were prepared in ca. 10 g batches.

1,4-bis(Bromodiphenylstannyl)butane (4a), purified by recrystallization from ether, was obtained in 75% yield: mp 88-90 °C. IR (Nujol): 1070 cm^{-1}. ^1H NMR: 1.71-1.93 (8 H, m), 7.17-7.67 (20 H, m).

1,5-bis(Bromodiphenylstannyl)pentane (4b) was obtained in 55% yield as an oil. IR (neat): 1070 cm^{-1}. ^1H NMR: 1.23-2.00 (10 H, m), 7.23-7.63 (20 H, m).

This reaction also gave 1-(bromodiphenylstannyl)-5-(triphenylstannyl)pentane as an oil in 5-10% yield. This product eluted after 4b. ^1H NMR: 1.30-1.93 (10 H, m), 7.23-7.70 (25 H, m).

1,6-bis(Bromodiphenylstannyl)hexane (4c) was isolated in 70-82% yield as an oil which crystallized on standing: mp 66-69 °C. IR (neat): 1070 cm^{-1}. ^1H NMR: 1.30-1.90 (12 H, m), 7.17-7.63 (20 H, m).

1,8-bis(Bromodiphenylstannyl)octane (4d) was obtained in 50-60% yield as an oil. IR (neat): 1070 cm^{-1}. ^1H NMR: 1.03-1.87 (16 H, m), 7.20-7.73 (20 H, m).

1,10-bis(Bromodiphenylstannyl)decane (4e) was obtained as an oil in 61% yield. IR (neat): 1072 cm^{-1}. ^1H NMR: 1.07-1.87 (20 H, m), 7.27-7.70 (20 H, m).

1,12-bis(Bromodiphenylstannyl)dodecane (4f) was obtained as an oil in 65-80% yield. IR (neat): 1073 cm^{-1}. ^1H NMR: 1.13-1.93 (24 H, m), 7.27-7.73 (20 H, m).

Preparation of dichlorides 8 are represented by the following preparation of 1,14-dichloro-5,5,10,10-tetraphenyl-5,10-distannatetradecane (8a). To a suspension of Mg (0.3 g, 12.5 mg-atom) in 10 mL of THF at -10 °C

was added over 40 min a solution of 1-bromo-4-chlorobutane (1.93 g, 11.2 mmol) in 30 mL of THF. The mixture was stirred for 30 min at 25 °C and 60 min at 0 °C. A one mL aliquot was titrated for active base (found 78% yield based on monometallation of the dihalide). The Grignard reagent solution was diluted with 30 mL of THF and transferred to a dry flask by cannula. To the Grignard reagent solution at 0 °C was added over 1.5 h a solution of 4a (3.0 g, 3.9 mmol) in 50 mL of THF (0.078 M). The reaction mixture was allowed to warm to 25 °C After 7 h at 25 °C, the reaction mixture was quenched with a satd aq NH_4Cl solution (50 mL). The organic layer was separated, and the aqueous layer was extracted with ether (2 x 50 mL). The combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), and reduced *in vacuo* to give an oily product (3 g). The crude product was purified by reverse phase chromatography with methanol elution to give 1.95 g (62%) of 8a as an oil. IR (neat): 1070 cm^{-1}. ^1H NMR: 1.03-1.87 (20 H, m), 3.44 (4 H, t, J = 7 Hz), 7.13-7.53 (20 H, m).

1,17-Dichloro-6,6,11,11-tetraphenyl-6,11-distannaheptadecane (8b) was prepared from 2.3 g (3 mmol) of 4b. The crude oily product was purified by reverse phase chromatography with CH_3CN/THF elution (6:1, v:v) to give 1.38 g (56% yield) of 8b as a colorless oil. IR (neat): 1072 cm^{-1}. ^1H NMR: 1.08-1.93 (26 H, m), 3.43 (4 H, t, J = 7 Hz), 7.17-7.53 (20 H, m).

1,20-Dichloro-7,7,13,13-tetraphenyl-7,13-distannaeicosane (8c) was prepared from 2.2 g of 4c (2.8 mmol). The crude product was purified by reverse phase chromatography with CH_3CN/THF elution (3:1, v:v) to give 1.85 g of 8c (60% yield) as an oil. IR (neat): 1070 cm^{-1}. ^1H NMR: 1.07-1.83 (32 H, m), 3.43 (4H, t, J = 7 Hz), 7.17-7.57 (20 H, m).

Syntheses of polystanna macrocycles were accomplished by three methods. Representative procedures are presented below for each method.

1,1,6,6-Tetraphenyl-1,6-distannacyclodecane (1a) and

5,5,6,6,11,11,16,16-octaphenyl-1,6,11,16-tetrastannacycloeicosane (2a) by the diGrignard method (Method A). To a suspension of 2 g of Mg (83 mg-atom) and a small crystal of I_2 in 50 mL of THF at 25 °C was added over 1 h a solution of 2.5 g of 1,4-dibromobutane (11.6 mmol) in 50 mL of THF. After stirring for 4 h, a 1 mL aliquot was titrated for active base (found: 85% of theory). The diGrignard reagent solution was separated from excess Mg by cannula transfer and was diluted to 200 mL (0.049 M) with THF, and the resulting solution was added over 2.5 h to a solution of 7.0 g of 4a (9.2 mmol) in 300 mL of THF at 0 °C. The reaction mixture was allowed to warm to 25 °C and was stirred for 10 h. The mixture was cooled to 0 °C, and saturated aqueous NH_4Cl solution (100 mL) was added. The organic layer was separated, and the aqueous layer was extracted twice with ether (70 mL). The combined ethereal solutions were washed with brine (2 x 50 mL), dried with $MgSO_4$, and filtered. The filtrate was reduced to give an oily product mixture which was purified by reverse phase chromatography with CH_3CN/THF elution to give 1.20 g of 1a and 1.58 g of 2a.

Compound 1a was recrystallized from hexane to give 1.03 g (17.2%) of colorless prisms: mp 114-114.5 °C (lit.[9] mp 96-98 °C). IR (Nujol): 1070 cm^{-1}. ^1H NMR: 1.37-1.50 (8 H, m), 1.57-2.03 (8 H, m), 7.23-7.60 (20 H, m). ^{13}C NMR: 140.6, 136.5, 128.4, 29.3, 10.1. Anal. Calcd for $C_{32}H_{36}Sn_2$: C, 58.41; H, 5.48. Found: C, 58.73; H, 5.42. MW: 654 (calcd for $C_{32}H_{36}Sn_2$ 657).

Compound 2a was recrystallized from a mixture of hexane/ether (3:1, v:v) to give 1.51 g (25.2%) of colorless prisms: mp 107.5-108 °C. IR (Nujol): 1070 cm^{-1}. ^1H NMR: 1.17-1.47 (16 H, m), 1.53-1.87 (16 H, m), 7.17-7.50 (40 H, m). ^{13}C NMR: 140.3, 136.7, 128.7, 128.4, 128.2, 31.6, 10.4. Anal. Calcd for $C_{64}H_{72}Sn_4$: C, 58.41; H, 5.48. Found: C, 58.06, H,

5.43. MW: 1341 (calcd for $C_{64}H_{72}Sn_4$: 1315)

1,1,7,7-Tetraphenyl-1,7-distannacyclododecane (1b) and 1,1,7,7,13,13,19,19-Octaphenyl-1,7,13,19-tetrastannacyclotetracosane (2b) were prepared by Method A from 0.66 g (2.8 mmol) of 1,5-dibromopentane and 1.6 g (2.06 mmol) of 4b. The crude product was separated by reverse phase chromatography with CH_3CN/THF elution (3:1, v:v) to give the desired macrocycles 1b and 2b.

Compound 1b was recrystallized from hexane to give 0.26 g (18.6 % yield) of 1b: mp 100-101 °C. IR (Nujol): 1070 cm^{-1}. ^1H NMR: 1.13-1.93 (20 H, m), 7.13-7.60 (20 H, m). Anal. Calcd for $C_{34}H_{40}Sn_2$: C, 59.53; H, 5.84. Found: C, 59.27; H, 5.78. MW: 664 (calcd for $C_{34}H_{40}Sn_2$: 686).

Compound 2b was repeatedly chromatographed (reverse phase) with CH_3CN/THF until the sample was pure by HPLC to give 0.3 g (21.4 % yield) of oily 2b which solidified on standing: mp 68-69 °C. IR (Nujol): 1070 cm^{-1}. ^1H NMR: 1.10-1.80 (40 H, m), 7.03-7.40 (40 H, m). Anal. Calcd for $C_{68}H_{80}Sn_4$: C, 59.53; H, 5.84. Found: C, 59.60; H, 5.84. MW: 1364 (calcd for $C_{68}H_{80}Sn_4$: 1371).

1,1,8,8-Tetraphenyl-1,8-distannacyclotetradecane (1c) and 1,1,8,8,15,15,22,22-Octaphenyl-1,8,15,22-tetrastannacyclooctacosane (2c) were prepared by Method A from 1.7 g (7 mmol) of 1,6-dibromohexane and 4.8 g (6 mmol) of 4c. The crude product was separated by reverse phase chromatography with CH_3CN/THF elution (3:1, v:v) to give the desired macrocycles 1c and 2c.

Compound 1c was recrystallized from hexane to give 1.13 g (26% yield) of 1c: mp 118-119 °C. IR (Nujol): 1073 cm^{-1}. ^1H NMR: 1.20-1.90 (24 H, m), 7.21-7.58 (20 H, m). ^{13}C NMR: 140.5, 136.6, 128.8, 128.1, 32.4, 25.4, 9.97. Anal. Calcd for $C_{36}H_{44}Sn_2$: C, 60.52; H, 6.21. Found: C, 60.20; H, 6.16. MW: 742 (calcd for $C_{36}H_{44}Sn_2$: 714).

Compound 2c was repeatedly chromatographed (reverse phase) with CH_3CN/THF elution until the sample was pure by HPLC to give 0.17 g (4% yield) of 2c as an oil. IR (neat): 1070 cm^{-1}. ^1H NMR: 1.10-1.87 (48 H, m), 7.20-7.60 (40 H, m). ^{13}C NMR: 140.4, 136.7, 128.3, 128.2, 33.7, 26.6, 10.5. Anal. Calcd for $C_{72}H_{88}Sn_4$: C, 60.52; H, 6.21. Found: C, 60.31; H, 6.17. MW: 1395 (calcd for $C_{72}H_{88}Sn_4$: 1427).

1,1,10,10-Tetraphenyl-1,10-distannacyclooctadecane (1d) and 1,1,10,10,19,19,28,28-octaphenyl-1,10,19,28-tetrastannacyclohexatricontane (2d) were prepared by Method A from 0.73 g (2.7 mmol) of 1,8-dibromooctane and 1.7 g (2.08 mmol) of 4d. The crude products were purfied by reverse phase chromatography with CH_3CN/THF elution (3:2, v:v).

Compound 1d was recrystallized from hexane (or CH_3CN/THF, 5:1, v:v) to give 0.4 g (25% yield) of 1d: mp 92-93 °C. IR (Nujol): 1072 cm^{-1}. ^1H NMR: 1.18-1.88 (32 H, m), 7.24-7.61 (20 H, m). Anal. Calcd for $C_{40}H_{52}Sn_2$: C, 62.35; H, 6.81. Found: C, 62.01; H, 6.72. MW: 743 (calcd for $C_{40}H_{52}Sn_2$: 770).

Compound 2d was repeatedly chromatographed (reverse phase) with CH_3CN/THF elution (3:2, v:v) until the sample was pure by HPLC to give 0.1 g (6.3% yield) of 2d which crystallized on standing: mp 70-71 °C. IR (Nujol): 1070 cm^{-1}. ^1H NMR: 1.10-1.77 (64 H, m), 7.13-7.50 (40 H, m). Anal. Calcd for $C_{80}H_{104}Sn_4$: C, 62.35; H, 6.81. Found: C, 62.06; H, 6.71. MW: 1494 (calcd for $C_{80}H_{104}Sn_4$: 1540).

1,1,12,12-Tetraphenyl-1,12-distannacyclododecane (1e) and 1,1,12,12,23,23,34,34-octaphenyl-1,12,23,34-tetrastannacyclotetratetracontane (2e) were prepared by Method A from 1.2 g (4 mmol) of 1,10-dibromodecane and 2.7 g (3.2 mmol) of 4e. The crude product was purified by reverse phase chromatography with CH_3CN/THF elution (1:1, v:v) to give the

desired macrocycles.

Compound 1e was recrystallized from hexane (or ethanol) to give 0.68 g (26% yield) of 1e: mp 86-87 °C. IR (Nujol): 1074 cm^{-1}. ^1H NMR: 1.20-1.90 (40 H, m), 7.23-7.60 (20 H, m). Anal. Calcd for $C_{44}H_{60}Sn_2$: C, 63.93; H, 7.32. Found: C, 64.05; H, 7.27. MW: 848 (calcd for $C_{44}H_{60}Sn_2$: 826).

Compound 2e was repeatedly chromatographed (reverse phase) with CH_3CN/THF (1:1, v:v) until the sample was pure by HPLC to give 0.18 g (7% yield) of 2e as an oil. IR (neat): 1070 cm^{-1}. ^1H NMR: 1.10-1.77 (80 H, m), 7.17-7.50 (40 H, m). Anal. Calcd for $C_{88}H_{120}Sn_4$: C, 63.93; H, 7.32. Found: C, 63.72; H, 7.28. MW: 1641 (calcd for $C_{88}H_{120}Sn_4$: 1652).

1,1,14,14-Tetraphenyl-1,14-distannacycloheracosane (1f) and 1,1,14,14,27,27,40,40-octaphenyl-1,14,27,40-tetrastannacyclodopentacontane (2f) were prepared by Method A from 1.7 g (5.2 mmol) of 1,12-dibromododecane and 3 g (3.4 mmol) of 4f. The crude products were purified by reverse phase chromatography with CH_3CN/THF elution (1:1, v:v).

Compound 1f was recrystallized from hexane (or ethanol) to give 0.72 g (24% yield) of 1f: mp 91.5-92 °C. IR (Nujol): 1075 cm^{-1}. ^1H NMR: 1.15-1.87 (48 H, m), 7.22-7.57 (20 H, m). Anal. Calcd for $C_{48}H_{68}Sn_2$: C, 65.31; H, 7.77. Found: C, 65.46; H, 7.73. MW: 913 (calcd for $C_{48}H_{68}Sn_2$: 882).

Compound 2f was repeatedly chromatographed (reverse phase) with CH_3CN/THF elution (1:1, v:v) until the sample was pure by HPLC to give 0.092 g (3% yield) of 2f as an oil. IR (neat): 1072 cm^{-1}. ^1H NMR: 1.07-1.83 (96 H, m), 7.20-7.60 (40 H, m). Anal. Calcd for $C_{96}H_{136}Sn_4$: C, 65.31; H, 7.77. Found: C, 65.38; H, 7.85. MW: 1709 (calcd for $C_{96}H_{136}Sn_4$: 1763).

Preparation of α,ω-bis(diphenyllithiostannyl)alkanes (7).[25] To a suspension of excess lithium metal (8-10 equivalents) and crushed glass in THF was added a solution of the appropriate 4 in THF (0.1-0.2 M) at room temperature. The mixture was heated under a gentle reflux for 0.5 h, and

then stirred at room temperature for an additional 8 h to give a dark green solution of the dilithium reagent 7. A 1 mL aliquot of the solution was titrated for active base,[23] but the end point of the titration was difficult to determine due to the color of the stannyllithium reagent solution.

Preparation of 1a by Method B. A solution of dilithium reagent 7a (1.58 mmol) in THF (50 mL, 0.032 M) was added over 1 h to a solution of 1,4-dibromobutane (5a) (1.7 mmol) in THF (100 mL, 0.017 M) at 0 °C. The reaction mixture was allowed to warm to room temperature. After stirring for 14 h, the resulting mixture was quenched, and the products were worked up by the procedure used in Method A. Purification of the crude product by reverse phase chromatography followed by recrystallization from hexane gave 0.46 g (42% yield) of 1a.

By similar procedures compounds 1b-1d were prepared by Method B. The yields of recrystallized products are given in Table 1.

Preparation of 2a by Method C. A solution of dilithium reagent 7a (1.88 mmol) in THF (50 mL, 0.022M) was added over 2 h to a solution of compound 8a (1.9 mmol) in THF (100 mL, 0.019 M) at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 18 h. The resulting mixture was quenched and worked up by the procedure used in Method A. Reverse phase chromatography and recrystallization from hexane/ether (3:1, v:v) gave 1.08 g (43% yield) of macrocycle 2a.

By similar procedures, compounds 2b and 2c were prepared by Method C. The yields of recrystallized products are given in Table 1.

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Table 1. Yields of Macrocyclic Products 1 and 2.

Compound	Ring Size	Isolated Yield (%)		
		Method A	Method B	Method C
1a	10	17	45	
1b	12	19	30	
1c	14	30	21	
1d	18	30	21	
1e	22	26		
1f	26	26		
2a	20	25	<2	43
2b	24	21	<2	33
2c	28	4	<2	33
2d	36	6		
2e	44	7		
2f	52	3		

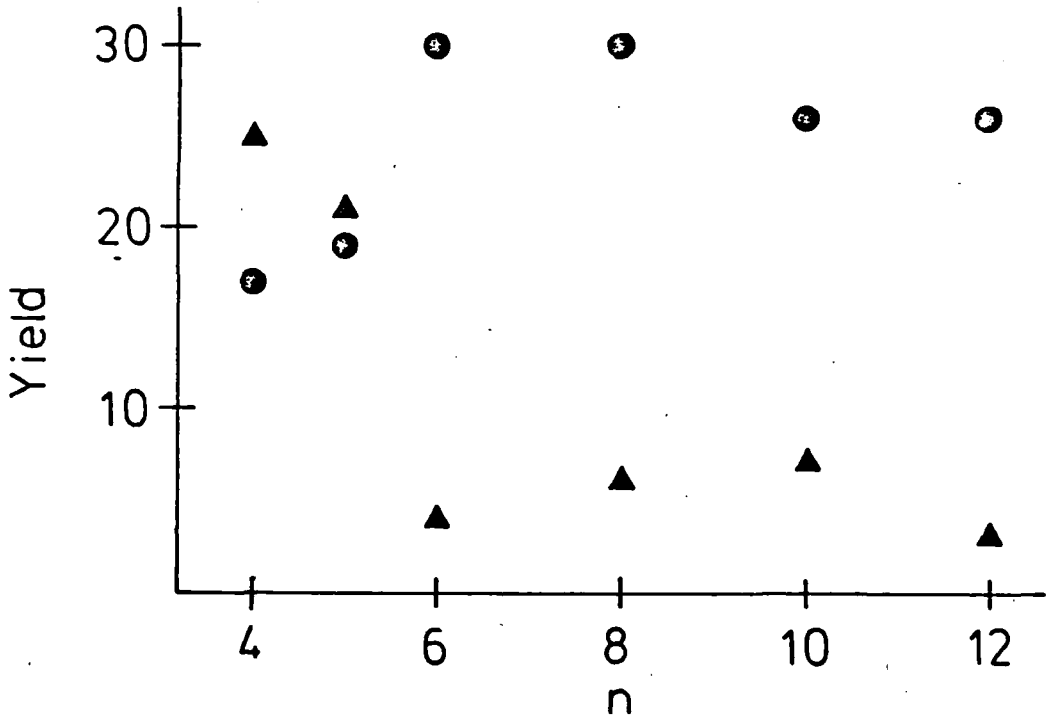
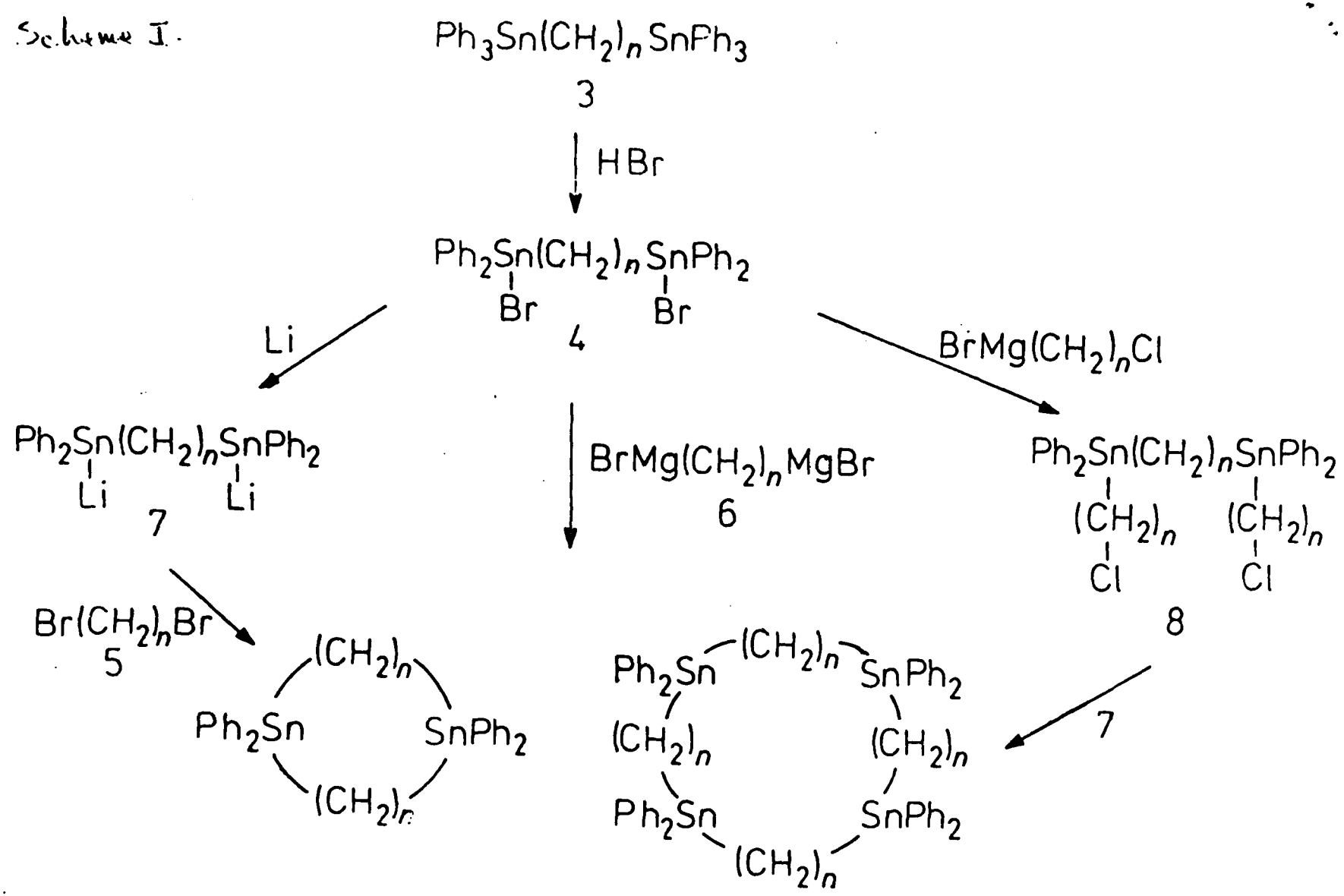


Figure 1. Percent isolated yield of bis(diphenylstanna)- (1, ●) and tetrakis(diphenylstanna)- (2, ▲) macrocycles as a function of carbon chain length (n).

Scheme I.



a n = 4
b n = 5
c n = 6
d n = 8
e n = 10
f n = 12

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