In summary, 8-arylbicyclo[4.2.0]octenediones, 2-aryl-2,3-dihydrobenzofurans, and/or 7-arylbicyclo[3.2.1]octenediones are formed enantiospecifically in reactions of various styrenes with quinones promoted by Ti(IV) complexes incorporating chiral ligands. The reactions are notable in that, to our knowledge, (a) these are the only direct, enantiospecific routes to ring systems of this type; (b) these include the first examples of asymmetric 5 + 2 cycloadditions promoted by an external chiral metal complex; and (c) they provide additional examples of asymmetric cyclobutane syntheses utilizing external chiral metal complexes.[4] In addition, four new contiguous asymmetric centers are formed in a single reaction.

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Supplementary Material Available: Representative experimental procedures for the preparation of **5**, **6**, **8**, and **11** in asymmetric form, selected physical and spectral data for (−)-**5**, (−)-**6a–c**, (+)-**6d/e**, (+)-**8d/e**, and (+)-**10** and full spectral data for the corresponding racemates, representative examples of NMR spectra used to establish % ee's, and summary of NOE data used to establish the stereochemistry of **5** (43 pages). Ordering information is given on any current masthead page.

Contribution of Nonbonded Interactions to the Destabilization of a Group 14 Bicyclo[1.1.1]pentane

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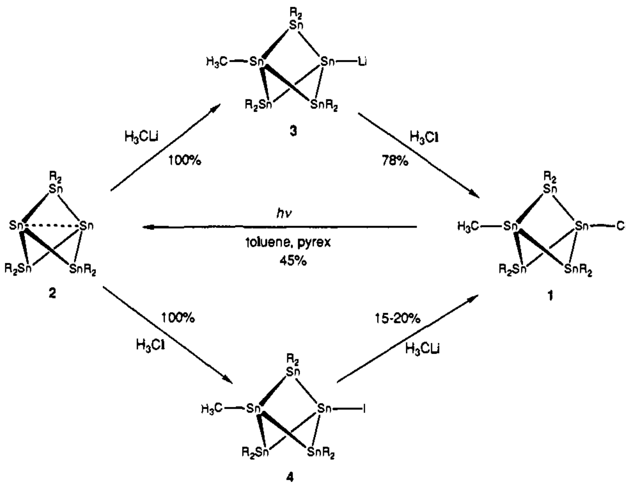
A current goal of group 14 chemistry is to develop modern structural theories for the heavier elements that can rival that for carbon in their ability to reliably predict stable and metastable atomic configurations on the potential energy surface of a given molecular system. In recent years, one approach toward this objective has been to obtain experimental structural parameters from the solid-state structures of a number of topologically interesting polycyclic compounds that possess M–M bonded frameworks (M = Si, Ge, and Sn) and to correlate them with the values predicted by molecular orbital calculations.[1,2] From these studies, it is now recognized that, while the correlation is generally high, nonbonded interactions between the bulky substituents used to "kinetically stabilize" synthetic derivatives can significantly contribute to structural discrepancies.[1e,2a] Herein, we report the synthesis of a bicyclo[1.1.1]pentastannane derivative, **1**, by two complementary routes, and its anomalous chemical and spectroscopic behavior, which further reveals how nonbonded interactions in synthetic derivatives of heavy-atom polycyclic compounds can influence another feature of theoretical interest, stability.

Scheme I[a]



[a] R = 2,6-diethylphenyl.

Synthesis of 1.[3] Addition of methyllithium (1 equiv) to a solution of 2,2,4,4,5,5-hexakis(2,6-diethylphenyl)pentastanna[1.1.1]propellane (**2**)[2j,k] in *n*-pentane quantitatively produces the adduct **3**, which can be isolated as an unstable pale-yellow crystalline material by cooling the reaction mixture to −40 °C (Scheme I). If, however, excess iodomethane is added to the initially formed solution of **3**, compound **1** can be obtained in a 78% overall yield. Alternatively, **1** can be produced by the addition of methyllithium to the 1-iodo-3-methylbicyclo[1.1.1]pentastannane derivative **4**,[2k] albeit in much lower yield (<20%) (Scheme I). With isotopically labeled reagents, this synthetic methodology has been used to prepare $[1\text{-}^{13}CH_3,99\%]$-**1** (**1a**) and $[1,3\text{-}^{13}CH_3,99\%]$-**1** (**1b**) as well.

Properties of 1. Compound **1** is an air-sensitive, yellow crystalline material which displays reversible thermochromic behavior by being nearly colorless at 77 K in a glass matrix (3-methylpentane) and in the solid state.[3] This observation correlates well with variable-temperature electronic spectra, which reveal that an absorption maximum, attributable to a $\sigma \rightarrow \sigma^*$ transition of the Sn–Sn bonded framework of **1**,[4] undergoes an apparent hypsochromic shift from 390 nm (ϵ 1000) at room temperature to 370 nm at 20 K. In the dark, solutions of **1** are indefinitely stable;[5] however, these solutions are sensitive to light, and quite

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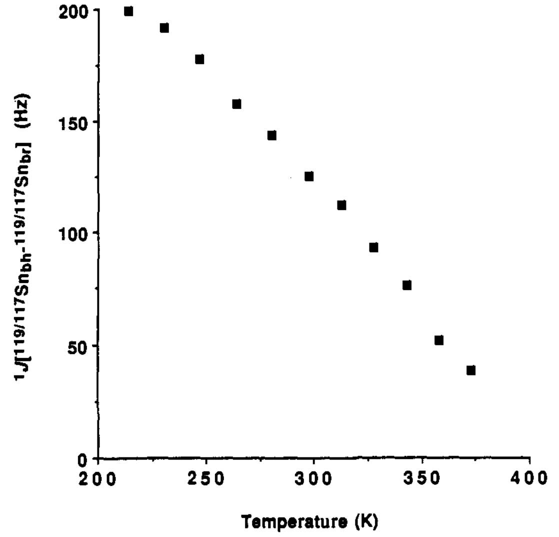

Figure 1. Temperature dependence of the one-bond coupling constant, $^{1}J[^{119/117}\mathrm{Sn_{bh}}-{}^{119/117}\mathrm{Sn_{br}}]$ (bh = bridgehead; br = bridging).

surprisingly, *photolysis (Hanovia medium-pressure lamp) for 3.5 h of a solution of **1** in toluene (c = 60 mM), sealed in a Pyrex tube, provided a 45% isolated yield of the pentastanna[1.1.1]propellane* **2** and at least trace amounts of ethane as determined by using **1a** and ^{13}C NMR spectroscopy (Scheme I). Since this photolytic production of **2** from **1** proceeds even in the presence of 2,3-dimethyl-1,3-butadiene, which is an efficient trapping reagent for R_2Sn,[6] a mechanism involving preferential stepwise (or concerted) homolytic cleavage of Sn–C_{Me} bonds rather than Sn–Sn bonds of **1** is suggested.[7] From space-filling models of **1**, it can be seen that a likely driving force for this process is the relief of nonbonded interactions between the 2,6-diethylphenyl ligands and the methyl substituents at the bridgehead tin atoms. Thus, the contribution of nonbonded interactions to the destabilization of the ground state of **1** facilitates a reaction pathway that could not be anticipated from the theoretical studies of the parent system, Sn_5H_8, alone.[1q,r]

NMR Spectroscopy of 1. A unique feature of the different valence-electron-mediated nuclear spin–spin coupling constants, *J*, of **1**, as extracted from ^{1}H, ^{13}C, and ^{119}Sn NMR (500, 125, and 186 MHz, respectively) spectra taken at 25 °C, is the relative ordering of $^{2}J[^{119}\mathrm{Sn_{bh}}-{}^{119}\mathrm{Sn_{bh}}]$, $^{2}J[^{119}\mathrm{Sn_{br}}-{}^{119}\mathrm{Sn_{br}}]$, and $^{1}J[^{119/117}\mathrm{Sn_{bh}}-{}^{119/117}\mathrm{Sn_{br}}]$, along with their absolute magnitudes, which are 7390, 1397, and 125 Hz, respectively.[8] We interpret the abnormally large values for the two-bond coupling constants, relative to those of acyclic compounds,[9] and the relative ordering of all three values as arising from additive contributions from multiple pathways, and perhaps from some transannular through-space interaction between the two bridgehead tin atoms in the case of $^{2}J[^{119}\mathrm{Sn_{bh}}-{}^{119}\mathrm{Sn_{bh}}]$.[10,11] In addition, the value for $^{1}J[^{119/117}\mathrm{Sn_{bh}}-{}^{119/117}\mathrm{Sn_{br}}]$, while apparently small, is in excellent agreement with the value expected from a correlation of $^{1}J[^{119}\mathrm{Sn}-{}^{119}\mathrm{Sn}]$ with Sn–Sn bond length.[4,12] What remains surprising, however, is that we found the absolute magnitude of this latter one-bond coupling constant to be dramatically temperature-dependent, starting at a value of 200 Hz at 214 K and decreasing to a value of 38 Hz at 373 K as shown in Figure 1.[3,13] With regard to the origin of this temperature effect, it has been previously noted that coupling constants can be temperature-dependent in stereochemically nonrigid systems where the observed value at a given temperature represents the relative contributions of different conformer populations which vary in the magnitude of the coupling constant.[10] Since in the present case the Sn–Sn bonded framework of **1** is stereochemically rigid, a dynamic intramolecular equilibrium process between two conformations can be ruled out. In addition, since compound **1** retains structural integrity in solution at elevated temperatures, as determined by NMR spectroscopy and trapping experiments,[14] and since the value of $^{1}J[^{119/117}\mathrm{Sn_{bh}}-{}^{119/117}\mathrm{Sn_{br}}]$ is not concentration-dependent, dynamic intermolecular equilibrium processes are probably not responsible. The most likely explanation for the temperature effect shown in Figure 1, therefore, is based on the assumption that, given the small force constants for Sn–Sn bond length and Sn–Sn–Sn bond angle distortions,[15] the Sn_5H_8 potential energy surface possesses a shallow minimum for the bicyclo[1.1.1]pentastannane structure. This implies that, at higher temperatures, compound **1** experiences cage deformations, such as a "breathing" mode expansion,[16] which are facilitated by an increase in the nonbonded interactions of the bulky substituents through torsional mobility and possibly, to some extent, by thermal population of vibrational excited states.[17] Hence, the dramatic change in the one-bond coupling constant of **1** can be seen as arising from ground-state destabilization that induces a positive displacement of the equilibrium $\mathrm{Sn_{br}}$–$\mathrm{Sn_{bh}}$ bond lengths and/or a change in the percent s character of the tin atoms due to changes in the $\mathrm{Sn_{bh}}$–$\mathrm{Sn_{br}}$–$\mathrm{Sn_{bh}}$ and $\mathrm{Sn_{br}}$–$\mathrm{Sn_{bh}}$–$\mathrm{Sn_{br}}$ angles at higher temperatures.[18] To the best of our knowledge, this is the first time that this type of temperature-dependent behavior has been observed for a *stereochemically rigid* polyatomic molecule by NMR spectroscopy.

In conclusion, we have shown in the present study that nonbonded interactions of sterically demanding substituents, which are typically used to kinetically stabilize reactive species, can, in fact, lead to destabilization. Thus, it can be anticipated that a fine balance of these interactions must be achieved in order to successfully isolate derivatives of heavy-atom group 14 polycyclic structures that possess reaction pathways with very low energy barriers, such as in the case of tetrasilatetrahedrane, Si_4H_4.[1n]

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(8) $|^{n}J[^{119}\mathrm{Sn}-{}^{119}\mathrm{Sn}]|$ determined from $|^{n}J[^{119}\mathrm{Sn}-{}^{117}\mathrm{Sn}]|_{\mathrm{obsd}} \times 1.046$ (see ref 9a); bh = bridgehead, br = bridging.

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(13) $^{2}J[^{119}\mathrm{Sn_{bh}}-{}^{119}\mathrm{Sn_{bh}}]$ and $^{2}J[^{119}\mathrm{Sn_{br}}-{}^{119}\mathrm{Sn_{br}}]$ are also temperature-dependent, but to a much smaller extent than $^{1}J[^{119/117}\mathrm{Sn_{bh}}-{}^{119/117}\mathrm{Sn_{br}}]$; see supplementary material.

(14) Heating solutions of **1** and 2,3-dimethyl-1,3-butadiene (3 equiv) showed no trace of the 1-stannacyclopentene product expected from reaction of the latter with thermally generated R_2Sn.

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Supplementary Material Available: Detailed information concerning the synthesis and variable temperature spectroscopic data of compounds **1**, **1a**, and **1b** (10 pages). Ordering information is given on any current masthead page.

Acid-Catalyzed Dehydration of Diols. Kinetic and Stereochemical Ramifications of Spirotetrahydrofuran Synthesis

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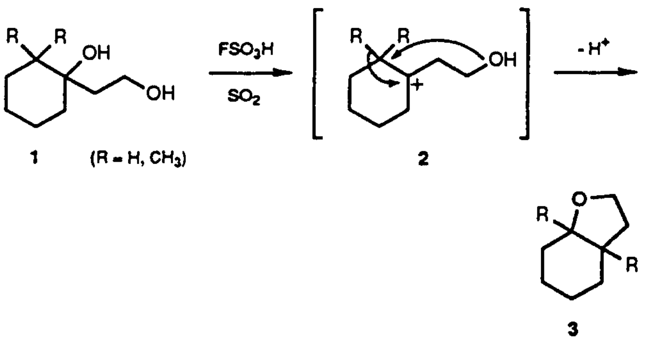
Carbocations play a major role in modern chemistry, and information linking structure to relative ease of ionization in the formation of these electrophilic species abounds.[1] Experiments showing the relative ease of carbocation generation to be tertiary > secondary > primary are detailed in all introductory texts.[2] At the next level, ditertiary diols are known to give rise to dications when dissolved in superacidic media.[3] Comparable treatment of 1-(2-hydroxyethyl)cyclohexanols, e.g., **1** (R = H, CH_3), results in kinetically controlled ionization to **2** and subsequent 1,2-hydride or -alkyl shift, setting the stage for ultimate cyclization to the perhydrobenzo[*b*]furan **3**.[4]



We herein report the discovery that acid-catalyzed dehydration of the homologous 1,4-diols **4** and **5**[5,6] can proceed under the proper circumstances with *high levels of stereochemical retention.* Our findings establish further that formation of the spirocyclic tetrahydrofurans **6** or **7**, respectively, proceeds by *selective displacement of the primary hydroxyl functionality without wholesale concurrent heterolysis of the tertiary C–O bond.* This striking reversal in the reactivity norm surfaces because of the large rate accelerations that can accompany the intramolecular displacement of protonated *primary* hydroxyl by *tertiary* hydroxylic oxygen.[7] This previously unappreciated kinetic factor can be attributed to the extensive operation of neighboring-group participation.[8] This cooperative pathway can become sufficiently preferred to permit useful stereoselectivities to be implemented.[9] Anionically driven intramolecular S_N' processes have recently been shown to hold substantial synthetic potential.[10]

Scheme I

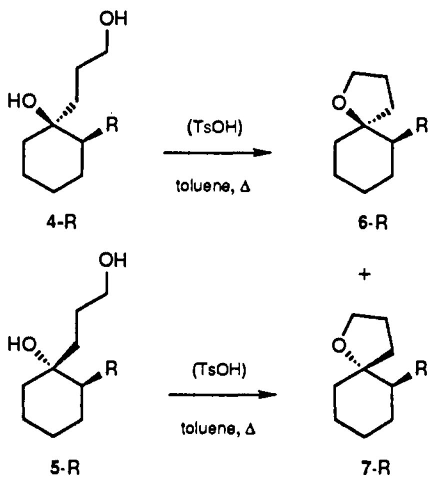


Table I. Stereochemical Consequences of Acid-Catalyzed Ring Closure Involving Diols **4** and **5**[a,b]

compd	**6**, %	**7**, %	compd	**6**, %	**7**, %
4-OCH_3	96	4	5-C_6H_5	55	45
5-OCH_3	8	92	4-CH_3	40	60
4-C_6H_5	67	33	5-CH_3	55	45

[a] Cat. TsOH, toluene, reflux. [b] Product analyses were determined by capillary GC analysis.

Table II. Extent of Retention of ^{18}O Following Acid-Promoted Cyclization of Specifically Labeled **4** and **5**[a]

starting diol	% ^{18}O at C-1	combined product yield, %	extent of isotopic label present, %	
			6	**7**
4-OCH_3	40	47[b]	40, 39	11[c]
5-OCH_3	39	52[b]	16[c]	38, 39
4-C_6H_5	45	84	20, 25	0, 0
5-C_6H_5	45	73	0, 0	19, 22
4-CH_3	39	68	9, 11	0, 0
5-CH_3	38	53	0, 0	6, 10

[a] Analyses performed by the ^{13}C NMR method described in the text. [b] Yields in these cases refer to major product only. [c] High-resolution mass spectral analysis made necessary because of limited quantities. Percentages obtained by analysis of *combined* minor products from duplicate runs.

We have analyzed the response of six diols to acid-catalyzed cyclization (Scheme I, Table I). The methoxyl derivatives **4**-OCH_3 and **5**-OCH_3 were examined first since (a) application of the Taft equation to limiting S_N1-type ionization of the proximate tertiary carbinol predicts that a 10^{-2} rate-retarding influence should be operative[11] and (b) the rate of ionization of *trans*-2-methoxycyclohexyl *p*-toluenesulfonate is known to be slowed approximately 100-fold.[12] Thus, electron-withdrawing electrostatic factors gain importance in these systems, while anchimeric as-

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(6) All new compounds reported herein have been fully characterized by 300-MHz ^1H and ^{13}C NMR spectroscopy and possess satisfactory C, H analyses and/or exact mass.

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