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Thermodynamic Control of 1,3-Boratropic Shifts of α- and γ-Stannyl-Substituted Allylboranes: Hyperconjugation Outweighs Steric Effects

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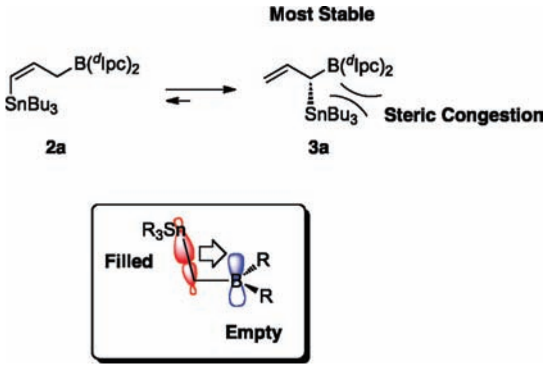
ABSTRACT



(*E*)-δ-Stannyl homoallylic alcohols are prepared by an allene hydroboration−aldehyde allylboration sequence (Chen, M. et al. *J. Am. Chem. Soc.* 2010, *132*, 7881). Key to this reaction sequence is that the kinetic allene hydroboration product, **2a**, is less stable than and isomerizes to the more sterically congested α-stannylallylborane **3a** (see abstract figure). An M06-2X density functional analysis shows that the C−Sn to boron *σ*−*π* hyperconjugation interaction is sufficiently stabilizing to override the steric congestion in **3a**.

The development of new carbonyl allylation reactions remain an important topic in organic synthesis.[1] These transformations are widely used in the stereoselective construction of C−C bonds with diverse substitution patterns.[1] Our laboratories recently demonstrated that an allenylstannane hydroboration−aldehyde allylation sequence generates (*E*)-δ-stannyl homoallylic alcohols with high enantioselectivity (Scheme 1).[2] This is an important contribution to this area because most allylation reactions generate products with terminal vinyl groups that often require several steps for further functionalizion.[3] Our previous experimental studies and computational analysis using the B3LYP density functional approximation (DFA) showed that (^{d}Ipc)$_2$BH addition to allene **1** first gives the (*Z*)-δ-stannylallylborane **2a** that then undergoes a rapid and highly diastereoselective 1,3-boratropic shift[4] to give **3a**.[2] Addition of an aldehyde to **3a** results in formation of the (*E*)-δ-stannyl homoallylic alcohol **4**. Homoallylic alcohol **5** was not formed in these experiments. That

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(1) (a) Roush, W. R. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, U.K., 1991; Vol. 2, p 1. (b) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207. (c) Denmark, S. E.; Almstead, N. G. In *Modern Carbonyl Chemistry*; Otera, J., Ed.; Wiley-VCH: Weinheim, 2000; p 299. (d) Chemler, S. R.; Roush, W. R. In *Modern Carbonyl Chemistry*; Otera, J., Ed.; Wiley-VCH: Weinheim, 2000; p 403. (e) Denmark, S. E.; Fu, J. *Chem. Rev.* **2003**, *103*, 2763. (f) Lachance, H.; Hall, D. G. *Org. React.* **2008**, *73*, 1.

(2) Chen, M.; Ess, D. H.; Roush, W. R. *J. Am. Chem. Soc.* **2010**, *132*, 7881.

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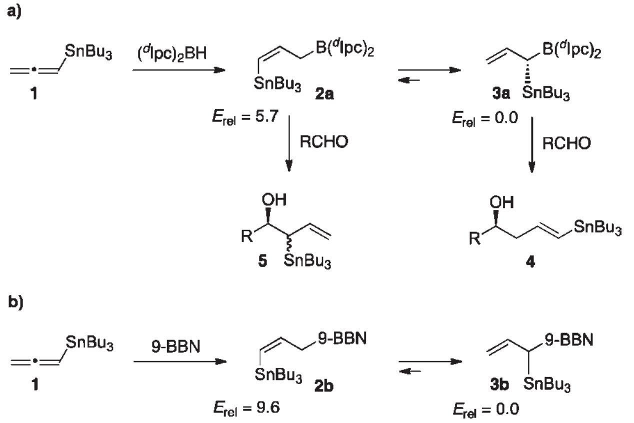
10.1021/ol2001599

Scheme 1. Allenestannyl Hydroboration−Aldehyde Allylation Reaction Sequence[a]



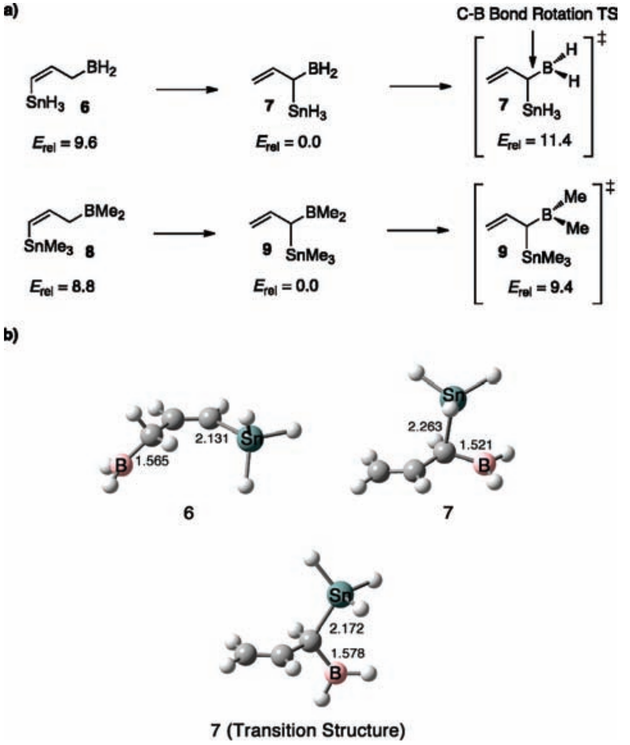
[a] M06-2X relative energies in kcal/mol.

intermediate **3a** is thermodynamically more stable than **2a** is somewhat surprising given that it places a bulky $-SnBu_3$ group geminal to the very bulky diisopinocampheylborane unit. Here we provide computational evidence that C−Sn σ-bond to boron p-orbital hyperconjugation is sufficiently stabilizing to overcome the steric congestion in **3a**.

B3LYP structures were optimized and verified as minima using Gaussian 03.[5] CCSD(T) energy calculations were also carried out in this Gaussian version. M06-2X energy evaluations were carried out in Jaguar 7.7[6] and Gaussian 09.[7] For geometry optimizations, the 6-31G(d,p) basis set was used for all atoms except Sn. The Gilbert and Sunderlin basis set was employed for Sn.[8] $SnBu_3$ groups were modeled as either $SnMe_3$ or SnH_3 groups. For energy evaluations, the larger LACV3P++** basis set was used with very dense grids.[9] Natural bond orbital (NBO) second-order perturbative delocalization energies (ΔE_{deloc}) were computed by comparison of the fully relaxed electronic structure (ΔE_{SCF}) with a localized Lewis bonding state (ΔE_{local}) using the keyword NBOdel in the NBO 3.1 program[10] attached to Gaussian 09. Although this perturbation technique does not partition the total energy of each molecule, it gives qualitative insights into relative electron delocalization energies.

To begin, we have also experimentally carried out the hydroboration reaction of allenylstannane **1** with 9-borabicyclo[3.3.1]nonane (9-BBN, Scheme 1b).[11] Similar to the (^{d}Ipc)$_2$BH hydroboration of allene **1**, allylborane **3b** is thermodynamically favored over the (*Z*)-alkene **2b**. Although the steric congestion would not be as severe in **3b** compared to **3a**, these results again illustrate that the geminal arrangement of C−Sn and C−B bonds is highly favorable.

Scheme 2. M06-2X 1,3-Boratropic Shift Thermodynamics and Transition-State Energies for C−B Bond Rotation of **7** and **9**[a]



[a] Distances are reported in angstroms.

Scheme 2 gives the computed thermodynamics for the 1,3-boratropic shifts of allylboranes **6** and **8**, which were used to model **2** and **3**. When the diisopinocampheyl and $SnBu_3$ groups of **2** are replaced with $-BH_2$ and $-SnH_3$ units to give **6** and **7**, the equilibrium determined by the M06-2X/LACV3P++** density functional approximation (DFA) shows that **7** is more stable than **6** by 9.6 kcal/mol

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(4) (a) Hancock, K. G.; Kramer, J. D. *J. Am. Chem. Soc.* **1973**, *95*, 6463. (b) Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1977**, *132*, 9. (c) Hoffmann, R. W.; Zeiss, H. J. *J. Org. Chem.* **1981**, *46*, 1309. (d) Henriksen, U.; Snyder, J. P.; Halgren, T. A. *J. Org. Chem.* **1981**, *46*, 3767. (e) Brown, H. C.; Jadhav, P. K.; Bhat, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 2564. (f) Wang, K. K.; Gu, Y. G.; Liu, C. *J. Am. Chem. Soc.* **1990**, *112*, 4424. (g) Gu, Y. G.; Wang, K. K. *Tetrahedron Lett.* **1991**, *32*, 3029. (h) Narla, G.; Brown, H. C. *Tetrahedron Lett.* **1997**, *38*, 219. (i) Fang, G. Y.; Aggarwal, V. K. *Angew. Chem., Int. Ed.* **2007**, *46*, 359. (j) Canales, E.; González, A. Z.; Soderquist, J. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 397. (k) González, A. Z.; Soderquist, J. A. *Org. Lett.* **2007**, *9*, 1081.

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(6) Jaguar, version 7.7, Schrodinger, LLC, New York, NY, 2010.

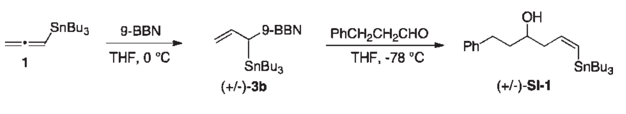
(7) Frisch, M. J. et al. Gaussian 09, Revision A.02; Gaussian, Inc.: Wallingford, CT, 2009. See the Supporting Information for full reference.

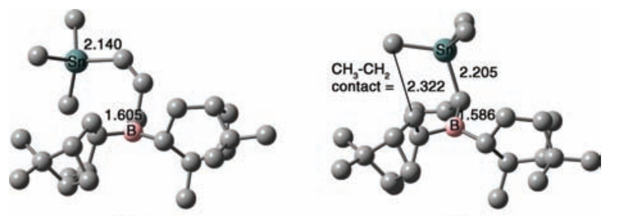
(8) Check, C. E.; Faust, T. O.; Bailey, J. M.; Wright, B. J.; Gilbert, T. M.; Sunderlin, L. S. *J. Phys. Chem. A* **2001**, *105*, 8111.

(9) Keywords gdftmed = −14, gdftfine = −14, and gdftgrad = −14 were used to generate a very dense grid.

(10) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO Version 3.1.

(11) Hydroboration of allenylstannane **1** (1 equiv) with 9-BBN (0.5 equiv) was carried out at 0 °C for 5 h. The structure of the resulting allylborane was deduced based on the allylboration product of hydrocinnamaldehyde. See the Supporting Information for details.



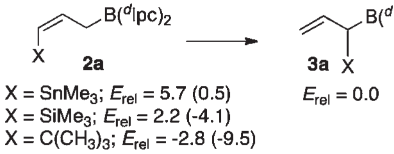


2a **3a**

Figure 1. Structures of **2a** and **3a**. Hydrogen atoms were removed for clarity. Distances are reported in angstroms.

(3D structures are shown in Scheme 2b). CCSD(T)/6-31G(d,p) theory predicts an almost identical energy difference of 9.5 kcal/mol and validates our use of M06-2X. The B3LYP DFA underestimates this energy difference by ~3 kcal/mol. When methyl groups are used rather than hydrogen atoms on the boron and tin units, the equilibrium between **8** and **9** still favors the geminal species **9** by 8.8 kcal/mol. Comparison of the energy difference between **6** and **7** or **8** and **9** with **2a** and **3a** shows that there is a ca. 4 kcal/mol decrease in the stability of the geminal species when bulky diisopinocampheyl and $SnMe_3$ groups are in close proximity (ΔE_{2a-3a} = 5.7 kcal/mol). Figure 1 shows that the $SnMe_3$ group is within ~2.3 Å of the isopinocampheyl groups.[12] The M06-2X energy difference between the hydroboration products of allene **1** and 9-BBN shows that the geminal species **3b** is favored by 9.6 kcal/mol over **2b** and indicates that the borabicyclo ring structure induces less steric congestion with the SnR_3 group.

Scheme 3. M06-2X/LACV3P++** Boratropic Shift Energetics[a]



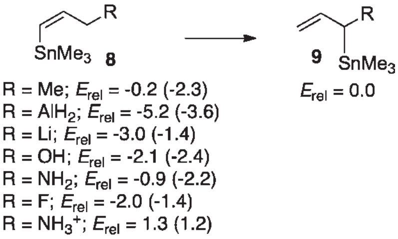
[a] B3LYP energies are given in parentheses.

We wondered whether this thermodynamic preference was unique for the SnR_3 group. Replacement of this group in **2a** and **3a** with $SiMe_3$ resulted in structure **3a** being favored by only 2.2 kcal/mol while replacement of the SnR_3 group with $C(CH_3)_3$ showed a 2.8 kcal/mol preference for structure **2a** (Scheme 3).

Because of the underestimation of this hyperconjugation effect, B3LYP predicted that for $SiMe_3$ and $C(CH_3)_3$ **2a** would be more stable than **3a**. A similar analysis on the 9-BBN structures, **2b** and **3b**, revealed a similar trend.

To test whether groups other than BMe_2 would also favor the geminal configuration, we computed the thermodynamics for replacement of the dimethylborane group in **8** and **9** with CH_3, AlH_2, Li, OH, NH_2, F, and NH_3^+ groups (Scheme 4). For nearly all of these units, structure **8** was found to be more stable than **9**. The only exception is the cationic ammonium group, which slightly favors the geminal structure. In fact, the AlH_2 group, which is isoelectronic with BH_2 does not favor structure **9**. This indicates that the geminal relationship of SnR_3 and BR_2 groups provides for a very unique stability that overrides steric congestion between the two groups.

Scheme 4. M06-2X/LACV3P++** Boratropic Shift Energetics[a]



[a] B3LYP energies are given in parentheses.

To understand the novel stability of structure **3a** (and model structures **7** and **9**), we have explored the possibility of hyperconjugative stabilization between the C−Sn σ-bond and the "empty" boron p-orbital. Figure 2a shows the C−Sn bond delocalization and interaction in a bonding and antibonding fashion with the boron p-oribital. This effect is similar to the well-known β-tin and β-silicon effects that stabilize radicals and cations.[13] The bond length differences between structures **2a** and **3a** (Figure 1) as well as **6** and **7** (Scheme 2b) show that when the C−Sn bond is geminal to the C−B bond it is elongated and the C−B bond is shortened. For example, in **6** the C−Sn bond is 2.131 Å and increases to 2.263 Å in **7**. The C−B bond lengths are 1.565 Å and 1.521 Å in **6** and **7**, respectively. Although the C−Sn bond length elongation can be rationalized by the increased steric congestion, the shorter C−B bond cannot.

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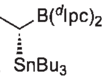
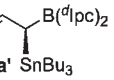
[12] Diastereoselective rearrangment of (*Z*)-δ-stannylallylborane **2a** can result in either **3a** or **3a′**. We previously showed (ref 2) that the 1,3-boratropic shift transition state leading to **3a** is 2.2 kcal/mol lower than the barrier leading to **3a′**. However, **3a′** is slightly more stable thermodynamically than **3a** (ca. 2:1 experimentally).



3a



3a'

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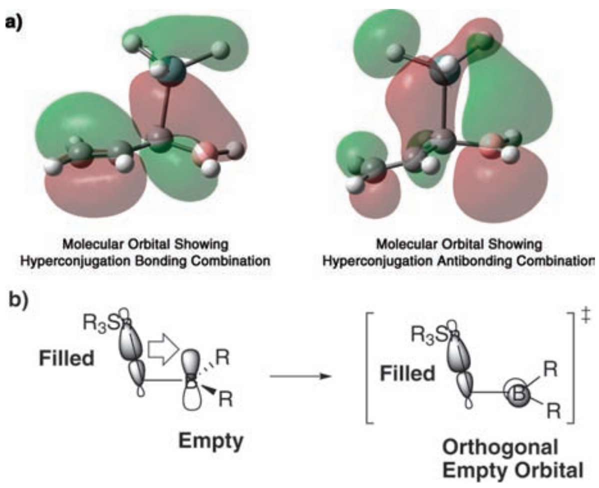

Figure 2. (a) Molecular orbitals showing the hyperconjugative interaction of C−Sn and boron p-oribtals. (b) Illustration of the diminished hyperconjugation interaction in the C-BR$_2$ bond rotation transition state.

This hyperconjugation hypothesis can also be inspected by computing the barriers for rotation about the C−BR$_2$ bond. Figure 2b illustrates that upon C−B bond rotation the boron p-orbital becomes orthogonal to the donor C−Sn bond. Indeed, in the transition structure for C−B bond rotation of structure **7** (Scheme 2b—right structure) the C−Sn becomes shorter with a bond length of 2.172 Å, and the C−B bond length increases to 1.578 Å, which is longer than the C−B bond length in **6**. Most important is that the transition structure for **7** requires an activation energy of 11.4 kcal/mol and for **9** requires 9.4 kcal/mol. These energy values are 1−2 kcal/mol larger than the energy of structures **6** and **8** and indicates that the hyperconjugation interaction that favors **7** and **9** has been severed and the C−Sn bond localized. As a comparison, the rotation barrier for replacement of the SnH$_3$ with a CH$_3$ group in **7** results in a barrier of only 1.3 kcal/mol. The Mulliken atomic charges for the Sn and B atoms also suggest charge delocalization. In **7**, the Sn and B charges are +0.51e and +0.14e. In the transition state for bond rotation, the charges on Sn and B are +0.55e and +0.24e, respectively. The NBO natural charges in structure **7** for Sn and B atoms are +1.30e and +0.28e and in the transition state are +1.31e and +0.54e. Both of these charge schemes show that the main difference is a significant decrease in charge on the boron center in the transition-state structure.

As another evaluation of the hyperconjugation interaction in structure **7** we have compared the NBO delocalization energies between **6** and **7** and compared this with the delocalization in the transition structure for bond rotation in **7**. NBO delocalization energies ($\Delta E_{\mathrm{deloc}}$) compare a localized bonding state with the fully delocalized state shown in Figure 2a. Although the molecular orbitals show the symmetry, of this interaction it does not indicate the energetic relevance of the interaction. The NBOdel keyword localizes the orbitals between two atomic centers and removes all donor−acceptor interactions, which would remove this hyperconjugative interaction. However, it is important to point out that this NBOdel procedure removes all donor−acceptor interactions.

The difference in delocalization energies ($\Delta\Delta E_{\mathrm{deloc}}$) between **6** and **7** is 50 kcal/mol. This number significantly overestimates the energy difference between **6** and **7** because it is a second-order perturbative analysis and does not partition to total SCF energy. However, this large delocalization energy is in accord with the work of Fernández and Frenking, who evaluated the intermolecular interactions in $[H_2C{-}CH(SnH_3)_2]^+$.[14] They found that the π-interactions that are dominated by two C−Sn bond to carbon p-orbital interactions are worth an estimated 60 kcal/mol of stability per interaction. Comparison of this energy to the difference in delocaliztion energies for when the SnH$_3$ group is replaced with CH$_3$ shows that the $\Delta\Delta E_{\mathrm{deloc}}$ value drops to only 10 kcal/mol. The $\Delta\Delta E_{\mathrm{deloc}}$ value for comparison of **7** and the transition structure for **7** shows a slightly larger difference of 60 kcal/mol. This confirms that the filled C−Sn bond to empty boron p-orbital donor−acceptor interaction is in large part responsible for the energy difference between **6** and **7**.

In conclusion, we have provided computational evidence that the hyperconjugative interaction between geminal C−Sn and C−B bonds is sufficiently stabilizing to overcome steric congestion in structures such as **2a**.

Acknowledgment. D.H.E. thanks BYU for financial support and the Fulton Supercomputing Center for computational support. W.R.R. thanks the NIH (GM038436) for support of this work at Scripps Florida.

Supporting Information Available. *XYZ* coordinates, absolute energies, and full Gaussian 03 and 09 references. This material is available free of charge via the Internet at http://pubs.acs.org.

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