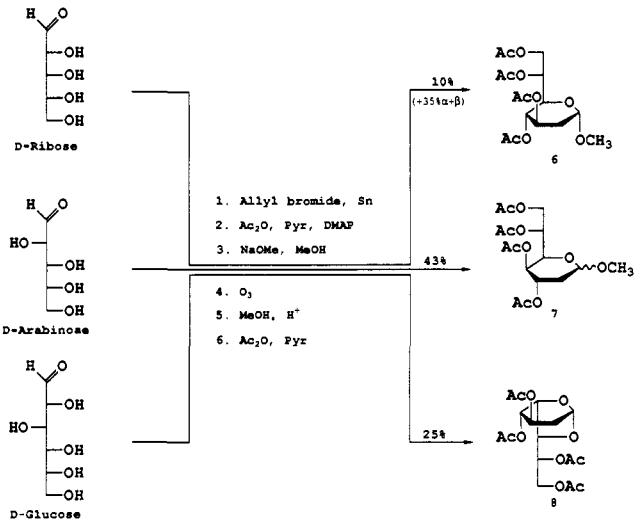
Table I. Nucleophilic Addition of Allyl Groups to Aldoses

starting carbohydrate	product[a]	yield,[b] %	diastereomeric ratio[c] (threo:erythro)
D-erythrose	**1**	52	4.0:1
D-ribose	**2**	65	3.5:1
D-arabinose	**3**	85	5.5:1
D-glucose	**4**	70	6.5:1
D-mannose	**5**	90	6.0:1
2-deoxy-D-glucose[d]		26	1.5:1
2-NAc-D-glucose		0	-
2-NAc-D-mannose		0	-

[a] Reactions were carried out in 9:1 ethanol/water with 2 equiv each of tin powder (100 mesh) and allyl bromide and promoted by ultrasonication until completion (12-16 h). [b] Based on isolated peracetylated diastereomers. [c] Determined from NMR. [d] Diastereomers not separated.

Scheme I. Conversions of D-Ribose, D-Arabinose, and D-Glucose to Heptose and Octose Derivatives **6**, **7**, and **8**



The yields reported in Table I were of isolated materials, following column chromatography over silica gel. Experimental details are given in supplementary material.

To assign the stereochemistry of the chiral center formed by addition of the allyl groups, we transformed three of the adducts (**2**, **3**, and **4**) to the corresponding heptose and octose derivatives **6**, **7**, and **8** by ozonolysis and appropriate derivatization (Scheme I). In the pyranose forms of these higher carbon sugars, the stereochemistry of the newly generated center could be assigned easily by analysis of coupling constants in the ^{1}H NMR spectra. For the major diastereomer formed in each reaction, the hydroxy function formed and that originally present at C-2 of the starting aldose have a threo relationship. This result is in agreement with observations made by Coxon et al.[12] for this type of reaction on aldehydes containing an asymmetric center adjacent to the carbonyl function. The diastereoselectivity is lower in the one case in which there is no hydroxy group present at C-2. For aldoses having *N*-acetyl groups in position 2, no reaction was observed under the reaction conditions used.[13]

This tin-promoted C-C bond forming reaction extends the range of synthetic methods applicable to unprotected sugars in protic solvents and should be especially useful in preparing higher carbon sugars. We are applying these methods to more highly functionalized systems and to other halide sources.

Supplementary Material Available: Experimental details for the preparation of **1-8** (7 pages). Ordering information is given on any current masthead page.

(12) Coxon, J. M.; van Eyk, S. J.; Steel, P. J. *Tetrahedron Lett.* **1985**, *26*, 6121-6124.

(13) This observation may suggest a possible complexation of the presumptive allyltin species to the α-hydroxy function.

On the Generation and Configurational Stability of (2*S*,3*S*)-1,2,3-Triphenylborirane

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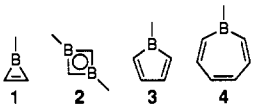
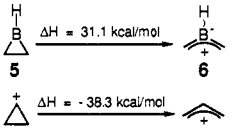
Received May 10, 1991

The isoelectronic analogy between an sp^2 boron atom and an sp^2 carbocation has stimulated both experimental and theoretical investigations of boracycloalkenes in search of Hückel aromatic or antiaromatic properties. Notable among these are the isolation and study of stable borirenes[1] **1**, 1,3-diboretanes[2] **2**, boroles[3] **3**, and borepines[4] **4**.



Our interest in this area is formulated in the possible valence isomerization of a borirane **5** to a boramethine ylide **6** by analogy to the isoelectronic cyclopropyl cation to allyl cation electrocyclic opening, eq 1. Indeed, thermal electrocyclic processes involving boron find precedent in the opening of 1-boranocaradienes[4d] and the closure of 1,3-dienylboranes.[5] In 1985 Schleyer et al.[6] reported that, unlike the highly exothermic opening of cyclopropyl cation (-38.3 Kcal/mol, 6-31G*), the disrotatory opening of borirane is predicted to be highly endothermic by 31.1 Kcal/mol (6-31G*//3-21G). We felt this energy gap could be reduced by appropriate substitution of the borirane as has been shown in the cyclopropyl cation case.[7]



Despite many early reports, simple boriranes[8] have never been

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(2) (a) Hildenbrand, M.; Pritzkow, H.; Zenneck, U.; Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 371. (b) Wehrmann, R.; Pues, C.; Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 372. (c) Schleyer, P. v. R.; Budzelaar, P. H. M.; Cremer, D.; Kraka, E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 374. (d) Krogh-Jespersen, K.; Cremer, D.; Dill, J. D.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 2589.

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(4) (a) Ashe, A. J. III; Drone, F. J. *J. Am. Chem. Soc.* **1987**, *109*, 1879. (b) van der Kerk, S. M.; Boersma, J.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1981**, *215*, 303. (c) Nakadaira, Y.; Sato, R.; Sakurai, H. *Chem. Lett.* **1987**, 1451. (d) Eisch, J. J.; Galle, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 4436. (e) Schulman, J. M.; Disch, R. L.; Sablo, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 7696.

(5) (a) Zweifel, G.; Backlund, S. J.; Leung, T. *J. Am. Chem. Soc.* **1977**, *99*, 5192. (c) Zweifel, G.; Hahn, G. R., Shoup, T. M. *J. Org. Chem.* **1987**, *52*, 5484.

(6) (a) Budzelaar, P. H. M.; Kos, A. J.; Clark, T.; Schleyer, P. v. R. *Organometallics* **1985**, *4*, 429. (b) Schleyer has recently calculated that the opening of 1-methylborirene is endothermic by 27.5 Kcal/mol. Bühl, M.; Schleyer, P. v. R.; Ibrahim, M. A.; Clark, T. *J. Am. Chem. Soc.* **1991**, *113*, 2466.

(7) (a) Sorensen, T. S.; Rauk, A. *Pericyclic Reactions*: Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. II, pp 3-16. (b) Radom, L.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8193.

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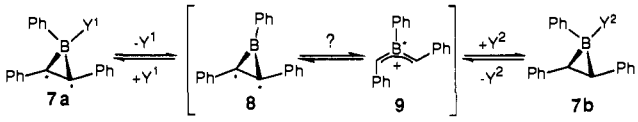
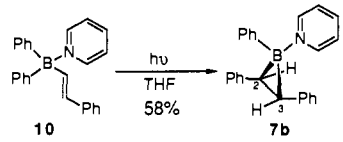
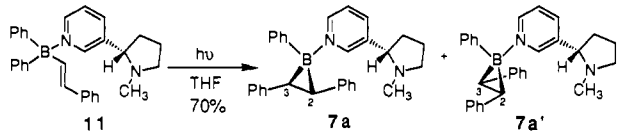
Scheme I



Scheme II



Scheme III

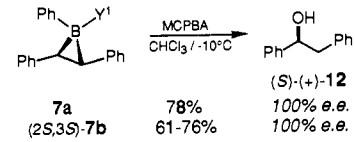


isolated nor detected, though their intermediacy has been postulated in reactions of borylenes with olefins.[9] Consequently, we have devised a stereochemical test for the generation and valence isomerization of a borirane. The concept requires the preparation of a chiral borirane ate complex **7a** (in scalemic form) bearing a nucleofugal ligand Y^1, Scheme I. Dissociation of Y^1 to the chiral borirane **8** sets up the critical test. Capture of **8** by a second ligand Y^2 produces a new complex **7b**. If **8** does not undergo electrocyclic opening, **7b** will retain the stereochemical information present in **7a** measured as an enantiomeric excess. However, if **8** does undergo competitive electrocyclic opening to achiral **9** then **7b** will lose some (or all) of that stereochemical information.[10]

Synthesis of the requisite borirane ate complexes proceeded by analogy to the elegant studies by Schuster on the di-π-methane rearrangement of alkenylborate salts.[11] For our purposes one of the aryl groups on boron was replaced with pyridine. Thus, direct irradiation of pyridinium diphenyl((*E*)-2-phenylethenyl)-borate (**10**)[12-14] afforded the air-sensitive *trans*-1-pyridinium 1,2,3-triphenylboratirane (**7b**)[14] as reddish-yellow prisms in 58% yield, Scheme II. The structure of **7b** was assured by the spectroscopic similarities to the tetraphenylboratirane analogue prepared by Schuster.[11a]

To obtain a 1,2,3-triphenylborirane complex in scalemic form we carried out a classical resolution of diastereomeric derivatives. The adduct of (*S*)-nicotine with diphenyl((*E*)-2-phenylethenyl)-borane **11**[14] underwent di-π-methane rearrangement upon direct irradiation to afford a 1/1 mixture of diastereomeric borirane ate complexes **7a** and **7a'** in quantitative yield (^{1}H NMR). One recrystallization from toluene afforded a 1.6/1 mixture of **7a** and **7a'** ion 70% yield, Scheme III. Further recrystallization of this mixture provided a pure sample of **7a**[14] (18% yield) that was >99% de by ^{1}H NMR analysis (S/N, 268/1). The absolute configuration of this diastereomer was shown to be (2*S*,3*S*) by X-ray crystallographic analysis (see supplementary material).

Scheme IV



Two critical control experiments were required. First, **7a** was digested in 1 N HCl, and the recovered (*S*)-nicotine was shown to be >97% ee ($[\alpha]^{26}_D$ −164.8 (0.626, $CHCl_3$)). Second, a sample of **7a** was oxidized with MCPBA[15] to afford (*S*)-(+)-1,2-diphenylethanol, **12**,[16] ($[\alpha]^{26}_D$ +53.3 (0.866, $CHCl_3$)) in 78% yield, Scheme IV. The enantiomeric excess of (+)-**12** was established to be 100%[17] by chiral HPLC analysis of the derived 1-naphthylcarbamate.[14] Thus, we had in hand an analytical protocol that accurately revealed the enantiomeric composition and absolute configuration of the ligand-exchanged product.

Orienting NMR experiments in pyridine-d_5 showed that **7a** could be converted to **7b** at elevated temperatures. Thus, heating **7a** in pyridine (0.09 M) in a sealed tube at 100 °C for 3 days or 150 °C for 0.5 h afforded **7b** in 45 and 36% yield, respectively, after recrystallization. Oxidation of these samples to **12** and HPLC analysis of the derived carbamates revealed that the ligand exchange had occurred with 100% retention of configuration.

Clearly, the borirane skeleton had maintained its configuration during the ligand substitution process. This outcome can be explained by *both* dissociative and synchronous substitution mechanisms. Kinetic analysis of the exchange reaction over a 20 °C range allowed the determination of the following activation parameters: E_a = 37.9 Kcal/mol, ΔH^* = 37.1 Kcal/mol, ΔS^* = 16.8 eu.[18] The large positive entropy of activation is consistent with a dissociative mechanism requiring the intermediacy of **8**. Therefore, the valence isomerization of **8** to **9** is not competitive with capture by solvent pyridine.

The thermal stability of **8** and its apparent resistance to opening were very surprising. Schleyer[6] calculated that borirane has 16 Kcal/mol higher strain energy than cyclopropane but 14 Kcal/mol lower strain energy than cyclopropyl cation (6-31G*). Nevertheless, the ring strain in borirane is manifest in the 17 Kcal/mol exothermic rearrangement to vinylborane. No such rearrangements were detected in the exchange reactions. The key distinguishing feature of sp^2 boron compared to a carbocation is that the boron is less electronegative and is a poorer π-acceptor. Thus, strategies for making the opening more facile should involve attaching electron-withdrawing substituents on the boron.

In summary we have provided experimental evidence for the generation and configurational stability of 1,2,3-triphenylborirane and its reluctance to suffer electrocyclic opening to a boramethine ylide. We are continuing to probe this possibility by extending the lifetime of **8** and by stabilizing **9** with other substituents.

Acknowledgment. We are grateful to the Procter and Gamble Company for financial support under the auspices of the University Exploratory Research Program. A.-M.F. thanks NSERCC for a postdoctoral fellowship. We also thank John A. Burke and Professor William H. Pirkle for assistance with the HPLC analyses, Dr. Scott R. Wilson for the X-ray crystallographic determination of **7a**, and Professor Gary B. Schuster for advice on the borate photochemistry and stimulating discussions.

Supplementary Material Available: Spectroscopic and analytical data for **7a** along with a listing of crystal and positional parameters, bond lengths and angles, and torsional angles for **7a** (13 pages). Ordering information is given on any current masthead page.

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(10) Other conceivable mechanisms of epimerization (e.g., C–B bond cleavage) are experimentally distinguishable.

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(13) Prepared by in situ complexation of diphenyl((*E*)-2-phenylethenyl)-borane with pyridine. Cf.: Koster, R.; Horstschäfer, H.-J.; Biner, P. *Liebigs Ann. Chem.* **1968**, *717*, 1.

(14) This compound was fully characterized by spectroscopic (^{1}H, ^{13}C, ^{11}B NMR, UV, $[\alpha]_D$) and analytical (±0.3%) methods.

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(16) Berti, G.; Bottari, F.; Ferrarini, P. L.; Macchia, B. *J. Org. Chem.* **1965**, *30*, 4091.

(17) Pirkle, W. H.; McCune, J. E. *J. Liquid Chromatogr.* **1988**, *11*, 2165.

(18) Reactions at 115, 120, 125, 130, and 135 °C were monitored by ^{1}H NMR in pyridine-d_5. First-order kinetic behavior was observed through at least four half-lives (R^2 > 0.99).