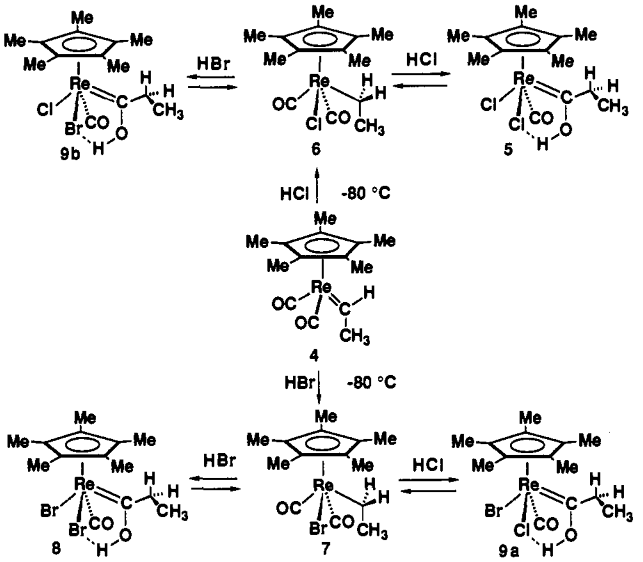
at δ 14.34, with a preferred conformation of the complex that results in long-range coupling of the OH proton to a single diastereotopic methylene proton of the ethyl group, and with the slow exchange of the OH group with excess HCl in CD_2Cl_2. The diastereotopic methylene protons of **5** establish the cis geometry of the complex.



The formation of hydroxycarbene complex **5** is reversible, and the equilibrium is shifted toward ethylchlororhenium complex **6** upon either warming or removal of HCl under high vacuum.

Reaction of **4** with 1.3 equiv of HBr led to the isolation of alkylbromo complex *cis*-$C_5Me_5(CO)_2BrReCH_2CH_3$ (**7**).[3] Reaction of excess HBr with either **4** or **7** at −80 °C led to the formation of the somewhat more stable hydroxycarbene complex $C_5Me_5(CO)Br_2Re{=}C(CO)CH_2CH_3$ (**8**),[3] which exhibits a doublet (J = 1.4 Hz) at δ 13.79 for the hydroxycarbene proton.

Remarkably, the reaction of HCl with *cis*-$C_5Me_5(CO)_2BrReCH_2CH_3$ (**7**) was stereospecific and produced a single diastereomer of $C_5Me_5(CO)BrClRe{=}C(OH)CH_2CH_3$ (**9a**)[3] with a hydroxy doublet at δ 14.30. The reaction of HBr with *cis*-$C_5Me_5(CO)_2ClReCH_2CH_3$ (**6**) produced a different diastereomer of $C_5Me_5(CO)BrClRe{=}C(OH)CH_2CH_3$ (**9b**)[3] with a hydroxy doublet at δ 13.83 in addition to a small amount of dibromo hydroxycarbene complex **8**. Synthesis of a mixture containing all four hydroxycarbene complexes **5**, **8**, **9a**, and **9b** showed four separate doublets for the hydroxycarbene protons.[5] On the basis of the hypothesis that the chemical shift of the OH proton is largely determined by the halogen to which it is hydrogen bonded, we have tentatively assigned the stereochemistry of the reaction as involving entry of the new halide ligand at a position cis to the hydroxycarbene ligand. The formation of these hydroxycarbene complexes is proposed to occur by migration of an alkyl group to a protonated carbonyl ligand with concerted attack of halide at rhenium. While Lewis acid[6] and Bronsted acid[7] induced alkyl migrations to CO are well known, the only prior example of Bronsted acid induced formation of a hydroxycarbene complex is the reaction of $(CO)_2(Ph_3P)_2Os(Cl)CH_2CH_3$ with HCl reported by Roper.[8]

In light of these findings, reinvestigation of the reaction of **1**-*d* with excess HCl in CD_2Cl_2 at −80 °C showed the formation of hydroxycarbene complex *cis*-$C_5H_5(CO)_2Cl_2Re{=}C(OH)$-$CHDCH_2CH_2CMe_3$ (**10**-*d*).[3] The deuterated alkyl group migrated with retention of stereochemical integrity to give one diastereomer of **10**-*d*. Upon warming to −30 °C, the equilibrium shifted back toward a single diastereomer of alkylrhenium complex **2**-*d*. This experiment demonstrates that the reversible formation of hydroxycarbene complexes is not related to the mechanism for loss of stereochemistry of **2**-*d*, which remains unresolved.

Acknowledgment. Financial support from the National Science Foundation and from the Department of Energy, Division of Basic Energy Sciences, is gratefully acknowledged.

Supplementary Material Available: Experimental details for the preparation and characterization of $C_5Me_5(CO)_2ReH^-K^+$ and compounds **4** to **10**-*d* (5 pages). Ordering information is given on any current masthead page.

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[5] Reaction of a 1:1 mixture of **6** and **7** with 0.5 equiv of HBr at −80 °C, followed by reaction with 3 equiv of HCl at −80 °C, produced a mixture of four hydroxycarbene complexes with distinct doublets in the ^1H NMR spectra at δ 14.34 (**5**), 14.30 (**9a**), 13.83 (**9b**), and 13.79 (**8**).

[6] Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 5093.

[7] (a) Butts, S. B.; Richmond, T. G.; Shriver, D. F. *Inorg. Chem.* **1981**, *20*, 278. (b) Forschner, T. C.; Cutler, A. R. *Organometallics* **1985**, *4*, 1247.

[8] Grundy, K. R.; Roper, W. R. *J. Organomet. Chem.* **1981**, *216*, 255.

Carbon–Carbon Bond Formation in Aqueous Ethanol: Diastereoselective Transformation of Unprotected Carbohydrates to Higher Carbon Sugars Using Allyl Bromide and Tin Metal[1]

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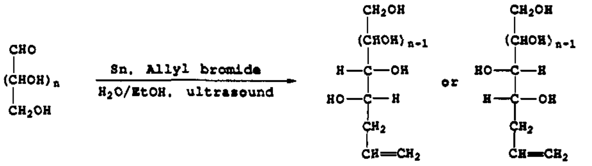
This report describes the "nucleophilic" addition of allyl groups to the carbonyl moieties of unprotected carbohydrates in aqueous/organic solvents (eq 1). These reactions are based on procedures developed and applied to non-sugar aldehydes and ketones by Luche,[3-6] Nokami,[7] Benezra,[8] and others[9,10] using reaction of allylic halides with zinc or tin metal in the presence of the carbonyl acceptor. When applied to carbohydrates, the reactions proceed with useful diastereoselectivity and permit the synthetic utilization of these water-soluble substrates directly in aqueous solutions without protection. The adducts were converted to higher carbon aldoses by ozonolysis of the deprotected polyols followed by suitable derivatization.



(1)

The yields reported in Table I were obtained in ethanol/water mixtures. Using tetrahydofuran instead of ethanol did not improve the yield but did slow the rate. Commercially available tin powder (Alfa company; 100 mesh) was used, and the suspension of the reactants was sonicated for 12–18 h in an ultrasonic cleaning bath (Cole-Parmer 8852).[11] Although the pH drops sharply during the course of the reaction (typically to a value of "pH" = 1), we did not run the reaction under positive pH control. The polyols generated were acetylated to simplify the purification procedure.

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[1] This work was supported by the NIH, Grant GM 30367.

[2] Erwin Schrödinger Postdoctoral Fellow of the Fonds zur Förderung der wissenschaftlichen Forschung in Österreich (Austrian Science Foundation).

[3] Einhorn, C.; Einhorn, J.; Luche, J. L. *Synthesis* **1989**, 787–813.

[4] Luche, C. J.; Damiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7926–7927.

[5] Petrier, C.; Luche, J. L. *J. Org. Chem.* **1985**, *50*, 912–915.

[6] Petrier, C.; Einhorn, J.; Luche, J. L. *Tetrahedron Lett.* **1985**, *26*, 1449–1452.

[7] Nokami, J.; Otera, J.; Sudo, T.; Okawara, R. *Organometallics* **1983**, *2*, 191–193.

[8] Mattes, H.; Benezra, C. *Tetrahedron Lett.* **1985**, *26*, 5697–5698.

[9] Wilson, S. R.; Guazzaroni, M. E. *J. Org. Chem.* **1989**, *54*, 3087–3091.

[10] Wu, S.; Huang, B.; Gao, X. *Synth. Commun.* **1990**, *20*(9), 1279–1286.

[11] Ultrasound increases the reactivity of many metals: Suslik, K. S.; Casadonte, J. D.; Doktycz, S. J. *Chem. Mater.* **1989**, *1*, 6–8. *Ultrasound: Its Chemical, Physical and Biological Effects*; Suslik, K. S., Ed.; VCH Publishers; New York, 1988. de Souza-Barboza, J. C.; Petrier, C.; Luche, J. L. *J. Org. Chem.* **1988**, *53*, 1212–1218.

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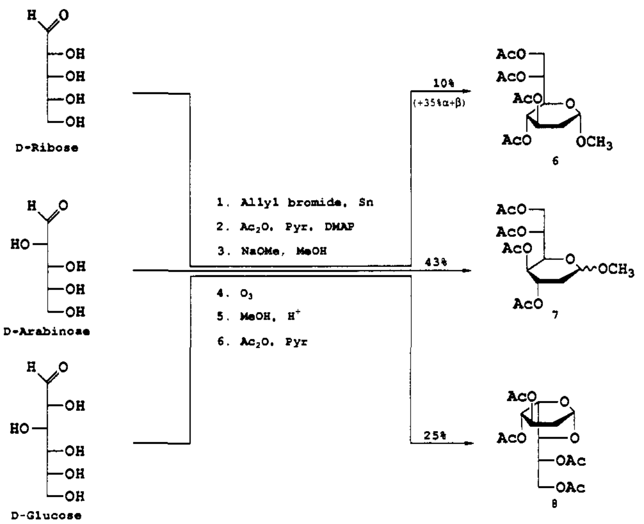
Table I. Nucleophilic Addition of Allyl Groups to Aldoses

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.

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(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**.


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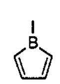
2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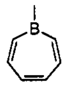
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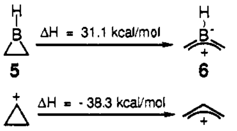
Our interest in this area is formulated in the possible valence isomerization of a borirane **5** to a boramethine ylide **6** by analogy to the isoelectronic cyclopropyl cation to allyl cation electrocyclic opening, eq 1. Indeed, thermal electrocyclic processes involving boron find precedent in the 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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(1) (a) van der Kerk, S. M.; Budzelaar, P. H. M.; van der Kerk-van Hoof, A.; van der Kerk, G. J. M.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 48. (b) Habben, C.; Meller, A. *Chem. Ber.* **1984**, *117*, 2531. (c) Pachaly, B. West, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 454. (d) Eisch, J. J.; Shafii, B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 2526. (e) Eisch, J. J.; Shafii, B.; Odom, J. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 1847.

(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.

(3) (a) Eisch, J. J.; Galle, J. E.; Kozima, S. *J. Am. Chem. Soc.* **1986**, *108*, 379. (b) Herberich, G. E.; Ohst, H. *Chem. Ber.* **1985**, *118*, 4303. (c) Fagan, P. J., Burns, E. G. Calabrese, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 2979.

(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.; Sabio, 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.

(8) 2-Borylideneboriranes have been prepared and studied by Berndt. (a) Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 877. (b) Wehrmann, R.; Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 369. (c) Lukasch, H.; Schmidt-Lukasch, G.; Lippold, U.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 960.

0002-7863/91/1513-6675$02.50/0