Pyrimidine is more electronegative than pyridine hence S–N-(pyrimidine) bond should be slightly longer and weaker than S–N(pyridine) bond according to the character of hypervalent bond.[3b] This trend is slightly enhanced by the electron-donating character of a methyl group (**1c**), and the rate is accelerated. On the other hand, the chlorine atom (**1d**) on the pyridine ring withdraws an electron to make the S–N(pyrimidine) bond shorter and stronger to recover the balance of the bond, hence the rate is decelerated. Again the bromine atom on the pyrimidine ring (**1e**) withdraws an electron to weaken the S–N(pyrimidine) bond more than that of **1a**. Monomethylpyrimidine derivative (**1f**: Me′ = H in **1a**) shows two kinds of the methyl signal between −48 °C and 35 °C, the ratio being 1.0:1.32 at 35 °C, and these coalesce at 45 °C.[8]

These can be visualized by difference of contribution of "no bond" resonance structures. As the electron-withdrawing property of the pyrimidino part increases compared to the pyridino part, the contribution of resonance structure (**1**-ii) will increase relative to **1**-iii, and therefore the S–N(pyrimidine) bond will be weakened. This is consistent with the (weak and polarizable) character of the hypervalent N–S–N bond which was predicted by the theoretical and structural analyses.[2,3]

A Diastereoselective Synthesis of (*E*)-Alkene-1,3-diols via the Reaction of 3-Borolenes with Aldehydes

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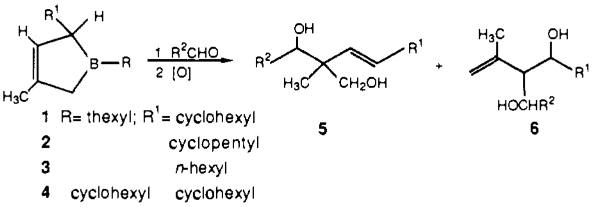
The development of new methods for acyclic stereocontrol is of major current importance in synthetic organic chemistry.[1] Topographical considerations have suggested that the bis-allylic 3-borolenes[2] might serve as templates for diastereoselective carbon–carbon bond-forming reactions in syntheses of acyclic compounds.[3] We now report an investigation of the reaction of 3-borolenes with aldehydes to provide stereodefined (*E*)-alkene-1,3-diols.[4] Specifically, the use of borolenes derived from isopropenyl acetylene (2-methyl-1-butene-3-yne) allows for extension of a carbon chain by one isoprene unit.

For our initial study the cyclohexyl-substituted borolene **1** derived from isopropenyl acetylene[5] was treated in THF with propanal, and the resultant organoboron intermediate was oxidized with alkaline hydrogen peroxide. ^{1}H NMR examination of the crude product mixture revealed the presence of the two regioisomeric diols **5a** and **6a** in a 98:2 ratio. As shown in Table I, the regioselectivity in the reactions of the thexyl-substituted borolenes **1–3** with aldehydes depends on the nature of the carbonyl compound used. Also, increasing amounts of the diols **6** are observed when the alkyl group R^1 at C$_2$ in **1** is sterically less hindered than cyclohexyl. This is especially evident in the case of the *n*-hexyl substituted borolene **3** which reacts with aldehydes in an essentially nonregioselective manner. Although the reaction of the cyclopentyl-substituted borolene **2** with propanal is less regioselective as compared to the cyclohexyl analogue, its reaction with *trans*-crotonaldehyde still furnishes mainly the corresponding diol **5f**.



Condensation of **1** with aldehydes is not only regioselective but also highly diastereoselective. Thus, GLC analysis of the crude mixtures of diols **5a–c** derived from various aldehydes indicated the presence of only one (>98%) out of the two possible diastereomeric diols. Single-crystal X-ray analysis established that the diols possess the relative configuration shown in **5a–c** (only one enantiomer is shown). To ascertain whether both diastereomeric diols if formed would indeed have been identifiable by GLC, **5a–c** were oxidized chemoselectively to the corresponding hydroxy ketones with Ag$_2$CO$_3$ on Celite.[6] Reduction of the hydroxy ketones with LiAlH$_4$ afforded mixtures of diastereomeric diols which could indeed be separated by GLC.[7]

The results obtained in the present study do not permit a definitive explanation of the regiochemistries and diastereoselectivities observed in the above carbon–carbon bond formation reactions to be made. However, as mentioned earlier, we have established that the regiochemistry is governed not only by the size of the 2-alkyl group on the borolene and by the nature of the aldehyde used but also, and very importantly, by the size of the alkyl group on boron. Thus, when the thexyl group on boron in **1** was replaced by the sterically less demanding cyclohexyl group and the resultant borolene **4** was reacted with propanal, a 54:46 ratio of the isomeric diols **5a** and **6a** was obtained. Hence, two regiochemically different pathways must be available by which borolenes react with aldehydes.

The preferential formation of diol **5** from the reaction of borolene **1** with various aldehydes may be envisioned to proceed via an initial anti coplanar complexation[8] of the carbonyl group syn to the R^1 group of the borolene giving **7a** or **7b**, respectively, in which the bulky thexyl group and the R^1 group are positioned away from each other. This allows the aldehyde to occupy a pseudoaxial position which is necessary for interaction with the p-orbitals of the borolene in the transition state for the subsequent reaction. Carbon–carbon bond formation between the trigonal centers of the aldehyde and the borolene should then, because of steric hindrance by the large cyclohexyl group (R^1), occur preferentially at the methyl-substituted carbon of the double bond.

The diastereoselectivity observed for the reaction may be rationalized by considering structure **7b**, where the H of the aldehyde is positioned between the C-5 of the borolene and the thexyl group. Rotation about the C=O axis of the aldehyde occurs in the direction that requires the least motion of the atoms involved for overlap of the p-orbitals participating in bond formation, as depicted in **8**.[9] This places the R^2 group over the trigonal centers

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(1) Evans, D. A.; Nelson, J. V.; Taber, T. R. *Top. Stereochem.* **1982**, *13*, 1. Heathcock, C. H. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3. Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1. Nõgrãdi, M. *Stereoselective Synthesis*; VCH Verlagsgesellschaft: Weinheim, Federal Republic of Germany, 1987.

(2) Zweifel, G.; Backland, S. J.; Leung, T. *J. Am. Chem. Soc.* **1977**, *99*, 5192.

(3) Recently, we have shown that 3-borolenes react with dimethyl sulfate and prenyl bromide to furnish substituted homoallylic alcohols. Zweifel, G.; Hahn, G. R.; Shoup, T. M. *J. Org. Chem.* **1987**, *52*, 5484.

(4) For leading references to reactions of acyclic allylic boranes with electrophiles, see: Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555. Yamamoto, Y.; Maruyama, K. *Heterocycles* **1982**, *18*, 357. Midland, M. M.; Preston, S. B. *J. Am. Chem. Soc.* **1982**, *104*, 2330. Masamune, S.; Choy, W.; Peterson, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1. Roush, W. R.; Halterman, R. L. *J. Am. Chem. Soc.* **1986**, *108*, 294. Jadhav, P. K.; Bhat, K. S.; Perumal, P. T.; Brown, H. C. *J. Org. Chem.* **1986**, *51*, 432.

(5) Shoup, T. M.; Zweifel, G. In *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds.; Elsevier: New York, 1986; Vol. 3.

(6) Oxidation of the diols **5a–h** with Ag$_2$CO$_3$ on Celite resulted in the nearly selective oxidation of the secondary hydroxyl groups. McKillop, A.; Young, D. W. *Synthesis* **1979**, 402.

(7) GLC examination of the diols **5d–h** coupled with the results of the oxidation–reduction procedure revealed that they were at least 96% diastereomerically pure. On the other hand, the diols **6** shown in Table I are diastereomeric mixtures whose stereochemistries have not yet been established.

(8) It has been shown that boron–carbonyl complexes adopt the anti coplanar structure. Reetz, M. T.; Hüllmann, M.; Massa, W.; Berger, S.; Rademacher, P.; Heymanns, P. *J. Am. Chem. Soc.* **1986**, *108*, 2405.

(9) A similar mechanistic scheme has been proposed for the reaction of chiral allenylboronic esters with aldehydes. Ikeda, N.; Arai, I.; Yamamoto, H. *J. Am. Chem. Soc.* **1986**, *108*, 483. Yamamoto, H.; Maruoka, K.; Furuta, K. In *Stereochemistry of Organic and Bioorganic Transformations*; Bartmann, W., Sharpless, K. B., Eds.; VCH Verlagsgesellschaft: Weinheim, Federal Republic or Germany, 1987; p 13.

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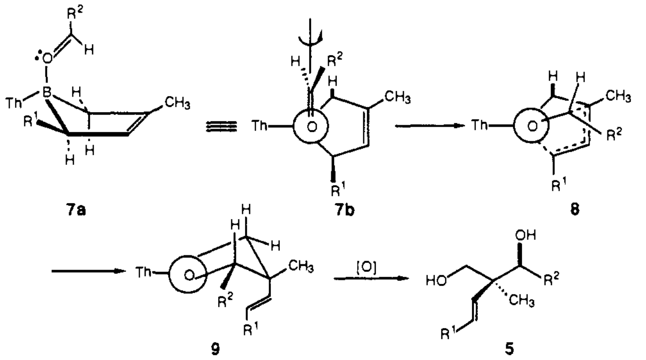
Table I. Regioselectivities Observed in Reactions of 3-Borolenes with Aldehydes

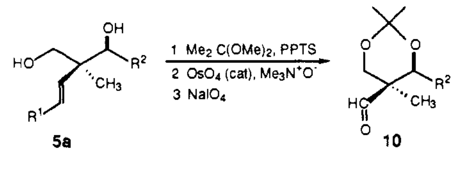
	3-borolene		R^{2}CHO		ratio of diols[a,b]		yield
	R	R^1	R^2		**5**	**6**	(%)
1	thexyl	cyclohexyl	C_2H_5	a	98	2	70
			i-C_3H_7	b	97	3	85
			$CH_3CH{=}CH$	c	99	1	82
2	thexyl	cyclopentyl	C_2H_5	d	80	20	75
			i-C_3H_7	e	53	47	81
			$CH_3CH{=}CH$	f	94	6	85
3	thexyl	*n*-hexyl	C_2H_5	g	54	46	72
			$CH_3CH{=}CH$	h	53	47	84
4	cyclohexyl	cyclohexyl	C_2H_5	a	54	46	89

[a] The ratio of the diols **5** and **6** were determined by GLC analysis of the crude reaction mixtures on a 30 m DB-210 J & W glass capilary column. [b] The IR and ^{1}H NMR data are consistent with the assigned structures.

of the borolene. It should be noted in this connection that steric interactions between R^2 and R^1 become less pronounced as bonding takes place between the aldehyde and the borolene since R^1 turns outward as C-2 becomes a vinylic carbon. Finally, carbon–carbon bond formation between the trigonal centers of the aldehyde and the borolene with concomitant formation of the trans carbon–carbon double bond leads to the 1,2-oxaborolane intermediate **9**. Oxidation of **9** with alkaline hydrogen peroxide affords the diol **5**.[10]



From a purely synthetic point of view, the presently reported preparation of regioisomerically and diastereomerically pure unsaturated diols **5** is confined to those having a cyclohexyl substituent at the vinylic carbon. However, it should be noted that oxidative cleavage of the double bond in the diols **5a**,**b** using the Lemieux–Johnson procedure,[11] which results in loss of the cyclohexyl moiety, should provide access to the more general stereodefined aldol products, as exemplified by the conversion of **5a** into the 1,3-dioxa-5-cyclohexanecarboxaldehyde (**10**) in 78% yield. These have a quaternary center which is not readily obtained by current methodologies.[12]



Acknowledgment. We thank Professor H. Hope for the X-ray crystallographic analyses of compounds **5a–c**, Professor R. W. Hoffmann (University of Marburg) for helpful discussions, and the National Science Foundation for financial support of this work.

Supplementary Material Available: Experimental details for the synthesis of compounds **1–6** (9 pages). Ordering information is given on any current masthead page.

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(10) We are grateful to a referee for valuable suggestions concerning the proposed mechanistic scheme.

(11) Pappo, R.; Allen, D. S.; Lemieux, R. U.; Johnson, W. S. *J. Org. Chem.* **1956**, *21*, 478. Ray, R.; Matteson, D. S. *Tetrahedron Lett.* **1980**, *21*, 449. Miyashita, M.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772. Kozikowski, A. P.; Stein, P. D. *J. Org. Chem.* **1984**, *49*, 2303. Wiesner, K.; Chan, K. K.; Demerson, C. *Tetrahedron Lett.* **1965**, 2893.

(12) Martin, S. F. *Tetrahedron* **1980**, *36*, 419.

Palladium-Catalyzed Asymmetric 1,4-Disilylation of α,β-Unsaturated Ketones: Catalytic Asymmetric Synthesis of β-Hydroxy Ketones

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We wish to report here a novel approach to optically active α-unsubstituted and α-anti-substituted β-hydroxy ketones[1] through palladium-catalyzed asymmetric 1,4-disilylation of α,β-unsaturated ketones followed by oxidative cleavage of the carbon–silicon bond (Scheme I).

In hopes of developing a new catalytic silylation of α,β-unsaturated carbonyl compounds,[2] we examined a variety of silylating reagents and catalysts for the reaction of 4-phenyl-3-buten-2-one (**1a**) and found that 0.5 mol% of tertiary phosphine–palladium complexes such as tetrakis(triphenylphosphine)palladium(0) catalyze the 1,4-addition of 1,1-dichloro-1-phenyl-2,2,2-trimethyldisilane ($Cl_2PhSiSiMe_3$)[3] under mild conditions (at 40–80 °C for 5–40 h). Treatment of the 1,4-disilylation product **2a** with an excess of methyllithium in ether followed by acidic hydrolysis of the resulting β-phenyldimethylsilyllithium enolate gave 4-phenyl-4-(phenyldimethylsilyl)butan-2-one (**3a**) in 70–80% yield (Scheme II). The pallladium-catalyzed disilylation was also observed with $Cl_3SiSiMe_3$, but $(MeO)_3SiSiMe_3$, $X_2MeSiSiMe_3$ (X = Cl, F), and symmetrically substituted disilanes such as $XMe_2SiSiMe_2X$ (X = F, Cl, Ph) did not react with **1a**.[4,5]

Enantioselective disilylation was effected with $PdCl_2$[(+)-BINAP][6] as a catalyst where BINAP stands for 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl.[7] The reaction conditions and

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(1) Although optically active α-syn-substituted β-hydroxycarbonyl compounds have been successfully prepared by the asymmetric aldol reaction, enantioselective synthesis of α-unsubstituted and α-anti-substituted β-hydroxy ketones remains to be explored. See, for example: (a) Narasaka, K.; Miwa, T.; Hayashi, H.; Ohta, M. *Chem. Lett.* **1984**, 1399. (b) Braun, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 24, and references cited therein. (c) Gennari, C.; Bernardi, A.; Colombo, L.; Scolastico, C. *J. Am. Chem. Soc.* **1985**, *107*, 5812. (d) Masamune, S.; Sato, T.; Kim, B.-M.; Wollmann, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 8279 and references cited therein.

(2) Fleming and co-workers have developed conjugate silylation of α,β-unsaturated carbonyl compounds with $(PhMe_2Si)_2CuLi$, which does not require any catalysts. (a) Fleming, I.; Goldhill, J. *J. Chem. Soc., Chem. Commun.* **1978**, 176. (b) Ager, D. J.; Fleming, I.; Patel, S. K. *J. Chem. Soc., Perkin Trans I* **1981**, 2520. (c) Fleming, I.; Newton, T. W. *J. Chem. Soc., Perkin Trans I* **1984**, 1805.

(3) Prepared by the chlorodephenylation of $Ph_3SiSiMe_3$ with dry HCl in the presence of $AlCl_3$ in benzene: Hengge, E.; Bauer, G.; Brandstaetter, E.; Kollmann, G. *Monatsh. Chem.* **1975**, *106*, 887. For the palladium–$Cl_2PhSiSiMe_3$ chemistry, see: Hayashi, T.; Yamamoto, A.; Iwata, T.; Ito, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 398.

(4) The disilylation with $Cl_2PhSiSiMe_3$ also occurred on different types of α,β-unsaturated ketones such as 3-methyl-4-phenyl-3-buten-2-one and 2-cyclohexenone: Hayashi, T.; Matsumoto, Y.; Ito, Y. *Tetrahedron Lett.*, in press.

(5) 1,4-Addition of $FMe_2SiSiMe_2F$ to methyl vinyl ketone in the presence of a palladium catalyst has been reported: Tamao, K.; Okazaki, S.; Kumada, M. *J. Organomet. Chem.* **1978**, *146*, 87.

(6) Prepared by mixing $PdCl_2(MeCN)_2$ with 1 equiv of (+)-BINAP in benzene and recrystallized from acetone/hexane: red crystal, mp 255–60 °C dec; $[\alpha]^{20}_D$ +682° (*c* 0.50, $CHCl_3$).

(7) Takaya, H.; Mashima, K.; Koyano, K.; Yagi, M.; Kumobayashi, H.; Taketomi, T.; Akutagawa, S.; Noyori, R. *J. Org. Chem.* **1986**, *51*, 629 and references cited therein.

0002-7863/88/1510-5579$01.50/0