

determined to be  $\beta$ -keto adipate. The implied operation of ortho cleavage<sup>6</sup> is the first report of this degradative pathway in *E. coli*.<sup>7</sup> Equivalents of D-glucose lost from the common pathway may thus be converted into  $\beta$ -keto adipate, which is then further metabolized. Diminished in vitro and in vivo availability of oxygen may limit enzyme-catalyzed reaction of catechol with oxygen, thereby allowing catechol to accumulate.

The conditions which induce DHS dehydratase and proto-catechuate decarboxylase in *E. coli* may not be directly applicable to other microbes. Nonetheless, any induction could have a deleterious effect on the percentage of D-glucose converted into desired product. This is of obvious concern in biocatalytic syntheses of L-phenylalanine,<sup>8</sup> L-tryptophan,<sup>9</sup> and indigo,<sup>10</sup> which generally attempt to increase the number of D-glucose equivalents channeled into the common pathway.

As a biocatalytic route to catechol, the induced pathway could be an alternative to the high temperatures, caustic solutions, metals, and peroxides used to chemically produce catechol.<sup>1</sup> An additional attractive feature of the discovered biocatalytic conversion is that D-glucose can be readily obtained from corn starch.<sup>11</sup> This contrasts with all other chemical<sup>1</sup> and biocatalytic syntheses<sup>12</sup> of catechol which utilize starting materials derived from nonrenewable fossil fuels.

(6) Stanier, R. Y.; Ornston, L. N. In *Advances in Microbial Physiology*; Rose, A. H., Tempest, D. W., Eds.; Academic: New York, 1973; Vol. 9, p 89.

(7) Meta cleavage has been observed in certain *E. coli* strains: (a) Burlingame, R.; Chapman, P. J. *J. Bacteriol.* **1983**, *155*, 113. (b) Burlingame, R. P.; Wyman, L.; Chapman, P. J. *J. Bacteriol.* **1986**, *168*, 55.

(8) Enei, H.; Hirose, Y. In *Comprehensive Biotechnology*; Moo-Young, M., Ed.; Pergamon: New York, 1985; Vol. 3, Chapter 27.

(9) Nakayama, K. In *Comprehensive Biotechnology*; Moo-Young, M., Ed.; Pergamon: New York, 1985; Vol. 3, Chapter 29.

(10) Ensley, B. D.; Ratzkin, B. J.; Osslund, T. D.; Simon, M. J.; Wackett, L. P.; Gibson, D. T. *Science* **1983**, *222*, 167.

(11) Reisman, H. B. *Economic Analysis of Fermentation Processes*; CRC: Boca Raton, 1988.

(12) (a) Nei, N.; Tanaka, T.; Takada, N. *J. Ferment. Technol.* **1974**, *52*, 28. (b) Nishimura, T.; Ishikawa, T. *Yukigoseikagaku* **1976**, *34*, 652. (c) Kuwahara, M.; Tsuji, M. *J. Ferment. Technol.* **1976**, *54*, 782. (d) Shirai, K. *Agric. Biol. Chem.* **1986**, *50*, 2875. (e) Shirai, K. *Agric. Biol. Chem.* **1987**, *51*, 121.

## Are Relative Bond Energies a Measure of Radical Stabilization Energies?<sup>1</sup>

K. Brady Clark and Danial D. M. Wayner\*

Organic Reaction Dynamics Group  
Steacie Institute for Molecular Sciences  
National Research Council of Canada  
Ottawa, Ontario, Canada K1A 0R6

Received June 24, 1991

Revised Manuscript Received September 19, 1991

It is a common perception that relative bond dissociation energies (BDE) are a measure of radical stabilization energies (RSE). This idea, which was proposed by O'Neal and Benson,<sup>2</sup> has been questioned by Rüchardt<sup>3</sup> and more recently by Nicholas and Arnold.<sup>4</sup> These authors pointed out that  $\Delta$ BDE values can be rationalized, alternatively, by considering the effect of substitution on the intrinsic stability of the molecule with its intact bond; i.e., a decrease in  $\Delta$ BDE may be the result of destabilization of the molecule rather than stabilization of the radical. Nicholas and Arnold<sup>4</sup> further noted that the  $\Delta$ BDE values obtained de-

Table I. Bond Dissociation Energy Data for Some Para-Substituted Benzyl Bromides<sup>a</sup>

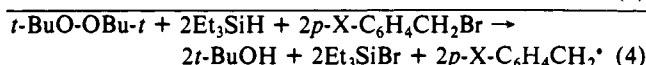
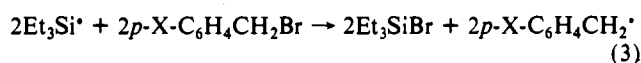
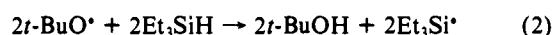
X	$\Delta$ BDE(X-C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> -Br) <sup>b</sup>
4-Me	0.34, 0.17
4- <i>t</i> -Bu	-0.34, 0.40
H	(0.0) <sup>c</sup>
4-F	-0.52
4-Br	-1.94, -1.74
4-CF <sub>3</sub>	-2.81
4-CN	-5.50, -4.52, <sup>d</sup> -4.07, -5.84

<sup>a</sup> Measured by photoacoustic calorimetry in triethylsilane/benzene (3:1 v/v). <sup>b</sup> Values represent the results of individual determinations. Each determination consists of at least eight pairs of measurements. <sup>c</sup> All values were determined relative to benzyl bromide (BDE = 59.4 kcal mol<sup>-1</sup>, ref 12c). <sup>d</sup> The photoacoustic constant ( $\alpha$ ) was measured from a plot of the signal amplitude versus the laser dose (see ref 8a).

ended on the nature of the R-X bonds that were compared and that  $\Delta$ BDE was a measure of RSE only for bonds with no net dipole moment.

While the limitations of this definition have been addressed, the concept, nevertheless, continues to pervade the recent literature. For example,  $\Delta$ BDE(O-H) values for a large number of substituted phenols in solution recently have been determined experimentally.<sup>5-7</sup> Bordwell and his co-workers attributed the bond energy differences to changes in the RSE, based on the assumption that the "effects of remote substituents on the ground state of parent molecules will be small compared to that on the radicals".<sup>7</sup> In this work we present evidence that leads us to the conclusion that the effect of remote substituents on the ground state of the parent molecules is important and, in some cases, may indeed be greater than that on the radicals.

We have used photoacoustic calorimetry to determine  $\Delta$ BDE values for a number of para-substituted benzyl bromides (Table I). This technique is described in detail elsewhere.<sup>8</sup> Briefly, argon-saturated solutions of the benzyl bromide and di-*tert*-butyl peroxide (1-12% v/v) in triethylsilane/benzene (3:1 v/v) were flowed through a standard flow cell and irradiated using a pulsed nitrogen laser (337.1 nm, 84.8 kcal mol<sup>-1</sup>, eqs 1-3). The net heat evolved from the overall photoreaction (eq 4) produced a shock wave that was detected using a piezoelectric transducer (microphone) that was in contact with the cell. The intensity of the shock wave is proportional to  $\Delta H^{\circ}_4$  when reactions 2 and 3 have lifetimes of <60 ns.<sup>5,9</sup> Using a value of  $k_2$  from the literature<sup>10</sup> and values for  $k_3$  measured by laser flash photolysis ( $k_3 > 10^8$  M<sup>-1</sup> s<sup>-1</sup>), we were able to determine the concentration range for each reactant that satisfied this time constraint.



(5) Mulder, P.; Saastad, O. W.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 4090.

(6) Lind, J.; Shen, X.; Eriksen, T. E.; Merenyi, G. *J. Am. Chem. Soc.* **1990**, *112*, 479.

(7) Bordwell, F. G.; Cheng, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 1736.

(8) (a) Clark, K. B.; Griller, D. *Organometallics* **1991**, *10*, 746. (b) Burkey, T. J.; Majewski, M.; Griller, D. *J. Am. Chem. Soc.* **1986**, *108*, 2218.

(9) (a) The rate constant for reaction of PhCH<sub>2</sub><sup>·</sup> with Bu<sub>3</sub>SnH is only ca.  $4 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup> (Franz, J. A.; Suleman, N. K.; Alnajjar, M. S. *J. Org. Chem.* **1986**, *51*, 19). Since the Sn-H bond energy is  $\approx 16$  kcal mol<sup>-1</sup> weaker than the Si-H bond, the reaction of the benzyl radicals with Et<sub>3</sub>SiH is expected to be too slow to contribute to the detected acoustic signals. (b) Under the experimental conditions the bromides do not absorb the incident light so the amplitude of the acoustic wave does not depend on the concentration of the bromide. (c) The  $\Phi$  value of 0.85 has been reported in the literature (Burkey, T. J.; Majewski, M.; Griller, D. *J. Am. Chem. Soc.* **1986**, *108*, 2218. Kanabus-Kaminska, J. M.; Hawari, J. A.; Griller, D. *J. Am. Chem. Soc.* **1987**, *109*, 5267).

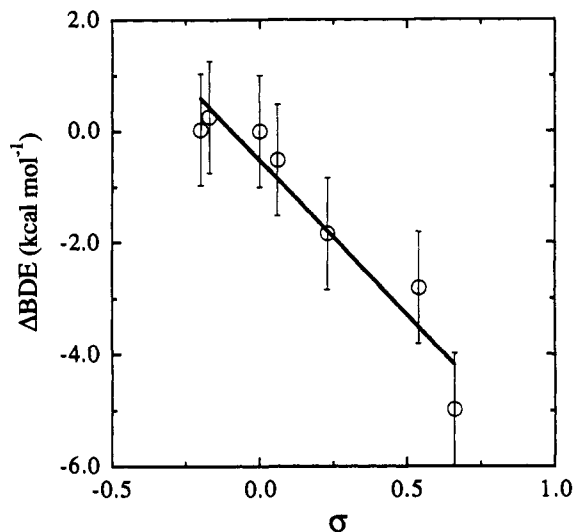
(10) Chatgililoglu, C.; Scaiano, J. C.; Ingold, K. U. *Organometallics* **1982**, *1*, 466.

(1) Issued as NRCC Publication No. 33254.

(2) O'Neal, H. E.; Benson, S. W. In *Free Radicals, Volume II*; Kochi, J. K., Ed.; Wiley: New York, 1973.

(3) Rüchardt, C. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 830.

(4) Nicholas, A. M. deP.; Arnold, D. R. *Can. J. Chem.* **1984**, *62*, 1850.

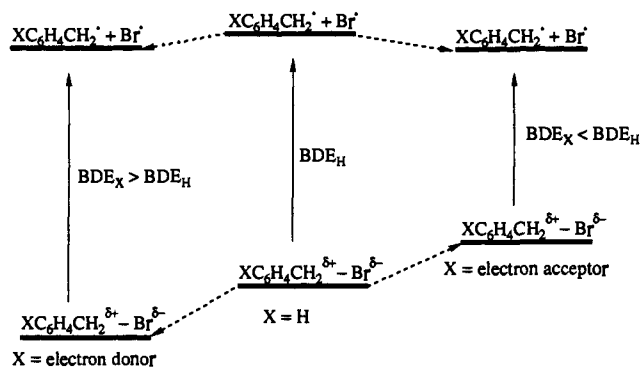


**Figure 1.** Plot of  $\Delta BDE$  for the para-substituted benzyl bromides versus  $\sigma$ . The points plotted are the average of the data for each substituent in Table I. The best fit line is defined by the equation:  $\Delta BDE = -0.5 - 5.5\sigma$  ( $r = 0.958$ ). The plot includes unsubstituted benzyl bromide which was used as a calibration standard. The Hammett  $\sigma$  values were those recommended by: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

All of the  $\Delta BDE$  values in Table I were measured relative to the unsubstituted benzyl bromide for which  $BDE(C-Br)$  is well-established.<sup>11-13</sup> By using the reaction of the unsubstituted system to calibrate the instrument it is possible to establish a simple relationship between the bond energy and the acoustic response (eq 5), where  $\alpha_X$  is the slope from a plot of the normalized photoacoustic signal versus the fraction of the incident light absorbed,  $\alpha_H$  refers to the corresponding slope for the unsubstituted compound, and the constant ( $81.5 \text{ kcal mol}^{-1}$ ) is a function of the energy of the absorbed light, the quantum yield for the photolysis of di-*tert*-butyl peroxide ( $0.85^8$ ) and the heats of formation of *t*-BuOOBu-*t*, *t*-BuOH,  $Et_3SiH$ ,  $Et_3SiBr$ , and  $Br^\bullet$ .<sup>12</sup> The precision of the measurements is typically  $\pm 1.0 \text{ kcal mol}^{-1}$  (e.g., four individual determinations for the 4-cyanobenzyl bromide over a four month period gave values with a standard deviation of  $\pm 0.7$ , Table I).

$$\Delta BDE (\text{kcal mol}^{-1}) = 81.5 (1 - \alpha_X/\alpha_H) \quad (5)$$

A plot of  $\Delta BDE$  versus  $\sigma$  is linear with a slope of  $-5.5$  ( $r = 0.958$ , Figure 1), i.e., electron-withdrawing substituents weaken the bond relative to the unsubstituted bromide. The direction of the effect is important since it has been shown<sup>14-17</sup> that the Hammett slope for the substituted toluenes is small but positive ( $< 2.0$ ), i.e., electron-withdrawing substituents strengthen the bond. Cleavage of the C-H bond in toluenes and cleavage of the C-Br



**Figure 2.** Energy level diagram depicting the effect of an electron-withdrawing group and electron-donating group on the relative BDEs of the C-Br bond in ring-substituted benzyl bromides.

bond in benzyl bromides both give the same product benzyl radical. It is clear, therefore, that in this case  $\Delta BDE$  is not a measure of RSE for the benzyl radicals. If that were the case then the sign and magnitude of the slopes of the two correlations would be the same. In fact, it is reasonably well-established that (with a few exceptions) both electron-withdrawing groups and electron-donating groups tend to stabilize this radical.<sup>18</sup> The differences in substituent effects on the  $\Delta BDE$ s for these two systems require that the substituent is exerting an important (i.e., greater) effect on the ground state of the parent molecule.

These results can be understood by considering the effect of the electron demand of the substituent on the intrinsic energy of the bond in the molecule. There are a number of mechanisms through which the substituent can interact with the C-Br bond. The two most important to consider are hyperconjugation (i.e., donation to the C-Br  $\sigma^*$  orbital) and substituent-dipole interactions.<sup>19</sup> The two mechanisms lead to similar predictions; the only difference between them being that the hyperconjugation mechanism has a conformational requirement (the C-Br bond must be aligned with the aromatic  $\pi$ -system). In systems such as the phenols (see below), this requirement is not met, and, until the need for the conformational preference is established, the more simple substituent dipole interaction mechanism should be preferred. For example, in the case of the benzyl bromide, the C-Br bond is polarized so that the carbon has a partial positive charge. When there is an electron-donating substituent on the aryl ring, the partial positive charge on the benzylic carbon is stabilized. This stabilizing interaction lowers the energy of the molecule and consequently increases the BDE (Figure 2). Conversely, an electron-withdrawing substituent destabilizes the partial positive charge on the benzylic carbon and decreases the BDE. Clearly, the magnitude of this effect will depend on the electronegativity difference of the atoms or groups in the bond being broken.

On the basis of these results it is essential to reconsider the origin of the substituent effects on the BDEs of the phenols.<sup>5-7</sup> Griller and his co-workers<sup>5</sup> reported that these values correlate with  $\sigma^+$  giving a slope of  $+7.3$ . Stein and his co-workers<sup>20</sup> measured the  $BDE(OCH_3)$  for a number of substituted anisoles (which also give phenoxyl radicals as products) and found that these data also correlate with  $\sigma^+$  but with a slope of only  $+2.9$ . The relative

(11) The  $BDE(C-Br)$  for benzyl bromide was established from  $\Delta H^\circ_f$  values in recent compilations.<sup>12</sup>

(12) (a) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. In *Thermochemical Data of Organic Compounds*; Chapman and Hall: New York, 1986. (b) Martinho-Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629. (c) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2. (d) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246. (e) Gordon, M. S.; Boatz, J. A.; Walsh, R. *J. Phys. Chem.* **1989**, *93*, 1584.

(13) A number of attempts were made to determine  $BDE(C-Br)$  for 4-methoxybenzyl bromide. However, this compound proved to be thermally unstable in the solvent mixture. Only a small amount of decomposition resulted in a background absorption at the laser wavelength that was sufficiently large that a reliable correction could not be made.

(14) Pryor, W. A.; Church, D. F.; Tang, F. Y.; Tang, R. H. In *Frontiers of Free Radical Chemistry*; Pryor, W. A. Ed.; Academic: New York, 1980; p 355.

(15) Zavitsas, A. A.; Pinto, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 7390.

(16) Gilliom, R. D. *J. Mol. Struct. (Theochem)* **1986**, *138*, 157.

(17) Wayner, D. D. M.; Sim, B. A.; Dannenberg, J. J. *J. Org. Chem.* **1991**, *56*, 4853.

(18) (a) Arnold, D. R. In *Substituent Effects in Radical Chemistry*; Viehe, H. E., Janousek, Z., Merényi, R., Eds.; Reidel: Dordrecht, The Netherlands; NATO ASI, Series C 1986, Vol. 189, p 171. (b) Creary, X. In *Substituent Effects in Radical Chemistry*; Viehe, H. E., Janousek, Z., Merényi, R., Eds.; Reidel: Dordrecht, The Netherlands; NATO ASI, Series C 1986, Vol. 189, p 245. (c) Timberlake, J. W. In *Substituent Effects in Radical Chemistry*; Viehe, H. E., Janousek, Z., Merényi, R., Eds.; Reidel: Dordrecht, The Netherlands; NATO ASI, Series C 1986, Vol. 189, p 271.

(19) A referee has suggested that differential solvation of the benzyl radicals compared to the bromides may account for part of the observed trends. While this possibility cannot be ruled out unequivocally, it has been shown for a number of other halides that gas-phase and solution bond energies are essentially the same (Castelhamo, A. L.; Griller, D. *J. Am. Chem. Soc.* **1982**, *104*, 3655).

(20) Suryan, M. M.; Kafafi, S. S.; Stein, S. E. *J. Am. Chem. Soc.* **1989**, *111*, 4594.

magnitudes of these slopes cannot be explained if only the effects on the radicals are considered. However, they are consistent with electronegativity differences between O-H and O-C in the bonds undergoing homolysis. In fact, a plot of the Hammett slopes for bond homolysis in the phenols,<sup>5</sup> anisoles,<sup>20</sup> toluenes,<sup>14</sup> and the benzyl bromides versus the electronegativity difference,  $\Delta V_X$ ,<sup>21</sup> appears to be linear with a slope of 2.0. While there is no reason to expect a linear relationship a priori, these trends clearly support the simple substituent-dipole interaction mechanism in Figure 2. The generality of this relationship is currently being explored.

The conclusion that remote substituent effects on bond energies reflect the interaction of the substituent with the dipole of the bond that is undergoing homolysis raises the following question. Is it possible to define radical stabilization energy so that it is both meaningful (i.e., a property of the radical only) and experimentally accessible?

**Acknowledgment.** The authors thank Professor J. M. Saveant for stimulating our interest in this work and Dr. K. U. Ingold for helpful discussions.

**Registry No.** 4-MeC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br, 104-81-4; 4-*t*-BuC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br, 18880-00-7; 4-FC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br, 459-46-1; 4-BrC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br, 589-15-1; 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br, 402-49-3; 4-CNC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br, 17201-43-3.

(21)  $V_X$  is a new electronegativity scale proposed recently by Luo and Benson.<sup>22</sup>  $\Delta V_X$  is the difference between the electronegativity of the atoms in the bond that undergoes homolysis (e.g.,  $V_C - V_B$  for the benzyl bromides and  $V_O - V_C$  for the anisoles).

(22) Luo, Y.-R.; Benson, S. W. *J. Phys. Chem.* **1989**, *93*, 4643, 3791, 3306, 3304, 1674. (b) Luo, Y.-R.; Benson, S. W. *J. Phys. Chem.* **1988**, *92*, 5255. (c) Luo, Y.-R.; Benson, S. W. *J. Am. Chem. Soc.* **1989**, *111*, 2480.

## New Catalysts for the Asymmetric Aldol Reaction: Chiral Boranes Prepared from $\alpha,\alpha$ -Disubstituted Glycine Arenesulfonamides

Emma R. Parmee, Orin Tempkin, and Satoru Masamune\*

Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

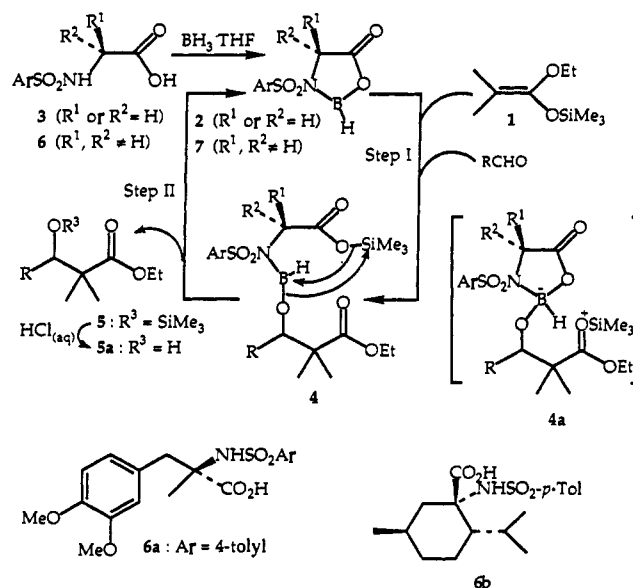
Atsushi Abiko

Institute for Fundamental Research, Kao Corporation  
Ichikai-machi, Haga-gun, Tochigi 321-34, Japan

Received August 1, 1991

The aldol reaction continues to attract the interest of synthetic organic chemists. One of the most recent versions involves the reaction of aldehydes with silyl ketene acetal 1, using the chiral Lewis acid mediator 2 prepared from BH<sub>3</sub>·THF and the sulfonamide derivative 3 of a natural  $\alpha$ -amino acid such as valine.<sup>1</sup> The efficient completion of this reaction with high enantioselectivity, however, requires a stoichiometric amount of 2, as we observed earlier, and efforts have been directed to the construction of a catalytic process<sup>2</sup> on the basis of the hypothetical Scheme I. Scheme I consists of steps I and II which involve (1) carbon-carbon bond formation to provide the initial aldol product 4 via 4a and (2) release of the silylated product 5 with simultaneous regeneration of 2, respectively.<sup>3</sup> Step II likely represents the

### Scheme I



slowest process and must be accelerated. Two obvious devices appear effective. (1) Use of synthetic  $\alpha,\alpha$ -disubstituted glycine arenesulfonamides 6 (neither R<sup>1</sup> nor R<sup>2</sup> is H) as shown in 7 would facilitate ring closure of 4 (as indicated by the arrows), a phenomenon commonly attributed to the Thorpe-Ingold effect.<sup>4</sup> (2) Slow addition of aldehydes to a mixture of 1 and 7 would reduce the accumulation of 4, a species which might also catalyze the aldol reaction but with a lesser enantioselectivity than that of 1. An enhancement of product enantiopurity is anticipated. Our investigation along this line of reasoning has resulted in catalytic asymmetric aldol processes which provide  $\beta$ -hydroxy esters 5a of >97% ee with typical primary aldehydes and 84-96% with secondary aldehydes.<sup>5</sup> The specific catalysts used are the borane complexes of 6a and 6b.

The first set of experiments concerned the  $\alpha$ -substituent effect of various ligands on the turnover capability of their borane complexes, as judged by the yield of the aldol reaction using a *substoichiometric* amount of the mediator. Thus, the *p*-toluenesulfonamides of several simple  $\alpha$ -amino acids provided the following results [the numbers in parentheses indicate the yields of 5a in the reaction using benzaldehyde (1 equiv), ketene acetal 1 (1.2 equiv), and mediators (20 mol %) prepared from BH<sub>3</sub>·THF and the *p*-toluenesulfonamides of amino acids]:<sup>6</sup> valine (54%), *tert*-leucine (46%),  $\alpha$ -methylalanine (95%), and  $\alpha$ -phenylalanine (98%).  $\alpha$ -Hydroxy carboxylic acids chosen for comparison gave similar results: malic acid (21%), mandelic acid (19%),  $\alpha$ -methylsuccinic acid (55%), and atrolactic acid (96%). The trend is consistent with the argument that disubstitution at the  $\alpha$ -carbon enhances the catalytic activity of the complexes, as outlined above.

(3) Earlier we observed that the neutral aqueous workup of the reaction mixture that resulted with 1 equiv of 2 (R<sup>1</sup> = isopropyl, R<sup>2</sup> = H) led to the isolation of the  $\beta$ -hydroxy ester 5a as the major product, indicating that the hydroxyl group of 5a was linked with B rather than Si. On prolonged standing, however, the reaction mixture became enriched in the silyl ether 5 of 5a as evidenced by its isolation.

(4) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc.* **1915**, 1080.

(5) For catalytic asymmetric aldol processes, see: (a) Ito, Y.; Sawamura, M.; Hayashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 6405. (b) Ito, Y.; Sawamura, M.; Shirakawa, E.; Hayashizaki, K.; Hayashi, T. *Tetrahedron Lett.* **1988**, *29*, 235. (c) Kobayashi, S.; Fujishita, Y.; Mukaiyama, T. *Chem. Lett.* **1990**, 1455. (d) Kobayashi, S.; Ohtsubo, A.; Mukaiyama, T. *Chem. Lett.* **1991**, 831 and references quoted therein. (e) Mukaiyama, T.; Inubushi, A.; Suda, S.; Hara, R.; Kobayashi, S. *Chem. Lett.* **1990**, 1015. (f) Mukaiyama, T.; Takashima, T.; Kusaka, H.; Shimpuku, T. *Chem. Lett.* **1990**, 1777. (g) Furuta, K.; Maruyama, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1991**, *113*, 1041; (h) Furuta, K.; Maruyama, T.; Yamamoto, H. *Synlett* **1991**, 439. (i) Reetz, M. T.; Kyung, S.-H.; Bolm, C.; Zierke, T. *Chem. Ind. (London)* **1986**, 824.

(6) Procedures as outlined in the text, except that the aldehyde was added neat over 1 min, followed by stirring at -78 °C (30 min) before quenching.

(1) Kiyooka, S.; Kaneko, Y.; Komura, M.; Matsuo, H.; Nakano, M. *J. Org. Chem.* **1991**, *56*, 2276.

(2) Chiral Lewis acids related to 2 are capable of catalyzing typical Diels-Alder reactions with good enantioselection. (a) Takasu, M.; Yamamoto, H. *Synlett* **1990**, 194. (b) Sartor, D.; Saffrich, J.; Helmchen, G. *Synlett* **1990**, 197.