has been presented. The former are obtained from the properties of a single temperature-independent transition state (a "substance") by conventional methods. The nonsubstantial contributions are obtained from more global properties of the potential energy surface (including the dependence of the variational transition state on temperature and quantum mechanical tunneling effects). An analysis of these contributions has been performed for five reactions for which the potential energy surface is known to give computed rate constants in excellent agreement with experiment. This analysis shows that the nonsubstantial contributions can be very significant; for example, for the OH + $H_2$ reaction the substantial and nonsubstantial contributions to the enthalpy of activation at 300 K are 4.8 and −3.8 kcal/mol, respectively, and for the O + $H_2$ reaction the substantial and nonsubstantial contributions to the entropy of activation at 300 K are −20.9 and −8.9 cal $mol^{-1}$ $K^{-1}$, respectively, for a standard state of 1 atm.

All the reactions studied here are hydrogen (or deuterium) atom transfer reactions with fairly high barriers (6–13 kcal/mol). For these reactions the nonsubstantial contributions are predominantly from quantum mechanical tunneling and the effect of variationally optimizing the location of the transition-state dividing surface is small. For reactions with smaller barriers we expect the effect of quantum mechanical tunneling to be smaller, but for those reactions the effects of variationally locating the dividing surface will become more important especially at higher temperatures.[48,49] It is therefore expected that the nonsubstantial contributions will be significant for a wide range of gas-phase chemical reactions.

The temperature dependence of both the substantial and nonsubstantial contributions to both the enthalpy and entropy of activation can be expressed in terms of temperature-dependent heat capacities of activation. This allows both contributions to the enthalpy and entropy of activation to be compactly tabulated in terms of their values at a single temperature (e.g., room temperature) and the temperature dependence given by the heat capacity of activation at several temperatures. This provides the basis for establishing a semiempirical data base, which includes important variational and tunneling effects in a thermochemical kinetic model.

**Acknowledgment.** This research was sponsored by SDIO/IST and managed by the Office of Naval Research under Contract N00014-87-C-0746 and was also supported in part by the U.S. Department of Energy, Office of Basic Energy Sciences, under Grant DE-FG02-86ER13579.

**Registry No.** H, 12385-13-6; D, 16873-17-9; O, 17778-80-2; OH, 3352-57-6; $H_2$, 1333-74-0; $D_2$, 7782-39-0.

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# Transition Structures for the Allylboration Reactions of Formaldehyde by Allylborane and Allylboronic Acid

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*Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90024-1569. Received May 2, 1988.*
*Revised Manuscript Received October 11, 1988*

**Abstract:** Chair and twist-boat transition structures for the reactions of formaldehyde with allylborane and allylboronic acid have been located with ab initio molecular orbital calculations and the 3-21G basis set. The relative energies of the transition structures were evaluated with the 6-31G* basis set. The twist-boat transition structure is predicted to be 8 kcal/mol less stable than the chair.

The stereocontrolled formation of carbon–carbon bonds is of great importance in organic synthesis.[1] Additions of allylic organometallic reagents to carbonyl compounds have been actively explored in recent years,[2,3] and the use of allylic organoborane reagents, in particular, has been shown to be a valuable method for the construction of carbon–carbon bonds with excellent control of stereochemistry.[3-5]

Allylic boranes and boronic esters undergo rapid reactions with carbonyl compounds. The products of these reactions arise from transfer of the rearranged allylic group from the metal to the carbonyl carbon ($S_E2'$ reaction). These products can then be easily converted into homoallylic alcohols or aldols, making this approach

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**Table I.** The 3-21G Optimized Bond Lengths (Å) and Bond Angles (deg) of the Stationary Points for the Reactions of Allylborane and Allylboronic Acid with Formaldehyde

| structures | bond lengths (Å) | | bond angles (deg) | | dihedral angles (deg) | |
|---|---|---|---|---|---|---|
| **1** | $R_{(\mathrm{C=C})}$ | 1.316 | ∠C=C—C | 124.8 | ∠C=C—C—B | 117.5 |
| | $R_{(\mathrm{C-C})}$ | 1.513 | ∠C—C—B | 114.2 | | |
| | $R_{(\mathrm{C-B})}$ | 1.582 | | | | |
| **2** | $R_{(\mathrm{C=C})}$ | 1.325 | ∠C=C—C | 125.5 | ∠C=C—C—B | -98.8 |
| | $R_{(\mathrm{C-C})}$ | 1.501 | ∠C—C—B | 111.2 | ∠C—C—B—O | 64.1 |
| | $R_{(\mathrm{C-B})}$ | 1.640 | ∠C—B—O | 101.8 | ∠C—B—O=C | -83.6 |
| | $R_{(\mathrm{B\cdots O})}$ | 1.685 | ∠C=O—B | 123.3 | | |
| | $R_{(\mathrm{C=O})}$ | 1.225 | | | | |
| **TS1** | $R_{(\mathrm{C=C})}$ | 1.353 | ∠C=C—C | 124.0 | ∠C=C—C—B | -84.2 |
| | $R_{(\mathrm{C-C})}$ | 1.455 | ∠C—C—B | 105.7 | ∠C—C—B—O | 56.9 |
| | $R_{(\mathrm{C\cdots B})}$ | 1.723 | ∠C—B—O | 100.6 | ∠C—B—O=C | -70.6 |
| | $R_{(\mathrm{B\cdots O})}$ | 1.565 | ∠C=O—B | 120.5 | ∠B—O=C—C | 65.7 |
| | $R_{(\mathrm{C=O})}$ | 1.266 | ∠C=C—C | 88.9 | ∠O=C—C=C | 53.9 |
| | $R_{(\mathrm{C\cdots C})}$ | 2.273 | ∠O=C—C | 102.6 | ∠C—C=C—C | 69.4 |
| **TS2** | $R_{(\mathrm{C=C})}$ | 1.358 | ∠C=C—C | 124.7 | ∠C=C—C—B | -70.7 |
| | $R_{(\mathrm{C-C})}$ | 1.446 | ∠C—C—B | 108.5 | ∠C—C—B—O | -8.4 |
| | $R_{(\mathrm{C\cdots B})}$ | 1.786 | ∠C—B—O | 103.6 | ∠C—B—O=C | 63.8 |
| | $R_{(\mathrm{B\cdots O})}$ | 1.546 | ∠C=O—B | 121.2 | ∠B—O=C—C | -53.1 |
| | $R_{(\mathrm{C=O})}$ | 1.278 | ∠C=C—C | 88.6 | ∠O=C—C=C | -10.4 |
| | $R_{(\mathrm{C\cdots C})}$ | 2.235 | ∠O=C—C | 108.4 | ∠C—C=C—C | 73.6 |
| **4** | $R_{(\mathrm{C1=C2})}$ | 1.316 | $\angle \mathrm{C_1C_2C_3}$ | 124.6 | $\angle \mathrm{C_1C_2C_3C_4}$ | 111.4 |
| | $R_{(\mathrm{C2-C3})}$ | 1.509 | $\angle \mathrm{C_2C_3C_4}$ | 110.8 | $\angle \mathrm{C_2C_3C_4O_5}$ | 177.1 |
| | $R_{(\mathrm{C3-C4})}$ | 1.530 | $\angle \mathrm{C_3C_4O_5}$ | 107.0 | $\angle \mathrm{C_3C_4O_5B_6}$ | 179.8 |
| | $R_{(\mathrm{C4-O5})}$ | 1.451 | $\angle \mathrm{C_4O_5B_6}$ | 126.5 | | |
| | $R_{(\mathrm{B6-O5})}$ | 1.366 | | | | |
| **TS3** | $R_{(\mathrm{C=C})}$ | 1.359 | ∠C=C—C | 123.3 | ∠C=C—C—B | 84.2 |
| | $R_{(\mathrm{C-C})}$ | 1.448 | ∠C—C—B | 105.3 | ∠C—C—B—O | -58.9 |
| | $R_{(\mathrm{C\cdots B})}$ | 1.708 | ∠C—B—O | 99.6 | ∠C—B—O=C | -70.6 |
| | $R_{(\mathrm{B\cdots O})}$ | 1.572 | ∠C=O—B | 118.5 | ∠B—O=C—C | 70.3 |
| | $R_{(\mathrm{C=O})}$ | 1.280 | ∠C=C—C | 89.8 | ∠O=C—C=C | 54.2 |
| | $R_{(\mathrm{C\cdots C})}$ | 2.176 | ∠O=C—C | 104.7 | ∠C—C=C—C | -68.8 |
| | $R_{(\mathrm{B-O})}$ | $1.451^a$ | ∠O—B—C | $109.5^a$ | ∠C—C—B—O | $-51.1^a$ |
| | $R_{(\mathrm{B-O})}$ | $1.423^b$ | ∠O—B—C | $112.7^b$ | ∠C—C—B—O | $174.3^b$ |
| **TS4** | $R_{(\mathrm{C=C})}$ | 1.364 | ∠C=C—C | 123.2 | ∠C=C—C—B | 56.0 |
| | $R_{(\mathrm{C-C})}$ | 1.444 | ∠C—C—B | 109.4 | ∠C—C—B—O | 25.6 |
| | $R_{(\mathrm{C\cdots B})}$ | 1.744 | ∠C—B—O | 101.3 | ∠C—B—O=C | -70.5 |
| | $R_{(\mathrm{B\cdots O})}$ | 1.551 | ∠C=O—B | 117.8 | ∠B—O=C—C | 45.2 |
| | $R_{(\mathrm{C=O})}$ | 1.295 | ∠C=C—C | 89.2 | ∠O=C—C=C | 22.8 |
| | $R_{(\mathrm{C\cdots C})}$ | 2.132 | ∠O=C—C | 110.0 | ∠C—C=C—C | -74.8 |
| | $R_{(\mathrm{B-O})}$ | $1.454^a$ | ∠O—B—C | $108.1^a$ | ∠C—C—B—O | $-84.6^a$ |
| | $R_{(\mathrm{B-O})}$ | $1.423^b$ | ∠O—B—C | $111.8^b$ | ∠C—C—B—O | $143.4^b$ |
| **TS5** | $R_{(\mathrm{C=C})}$ | 1.404 | ∠C=C—C | 119.4 | ∠C=C—C—B | -49.0 |
| | | | ∠B—C—C | 65.9 | | |

[a] Pseudo-axial oxygen on boron. [b] Pseudo-equatorial oxygen on boron.

a useful alternative to the aldol reaction. The observed rearrangement of the allyl moiety during the reaction has led to the conclusion that the addition of the allylic boron reagent to the carbonyl substrate proceeds through a cyclic six-center transition state.[6] A high degree of stereospecificity is observed with respect both to the *E–Z* configuration of the double bond of the allylic organoborane and to a chiral center α to the carbonyl of the substrate.[3,4] Recently, several groups have demonstrated that the use of chiral auxiliaries attached to boron can lead to additional products in high enantiomeric excess.[5] These stereochemical results have been rationalized in terms of a chairlike six-center cyclic transition state. In order to develop a more quantitative understanding of these stereoselectivities, we have located theoretical transition structures for the reactions of formaldehyde with allylborane and allylboronic acid.

## Computation Method

Ab initio molecular orbital calculations were carried out with Pople's GAUSSIAN 82 programs.[7] Geometries were optimized by using the Berny optimization program with gradient calculations.[8] We used the forming CC bond as the reaction coordinate and searched several points with constraints of the forming CC bond. Then, the point of highest energy was chosen as a trial geometry for the transition state optimization (OPT = TS). Transition structures were located by reading in the force constants (Hessian matrix) from the checkpoint file obtained by vibrational frequency calculations on the trial geometries at the STO-2G level. For the reaction of formaldehyde with allylborane, each stationary point was fully optimized with the 3-21G basis set[7] and characterized according to the eigenvalues of the final force constant matrix. The minima corresponding to reactants, the complex, and the products have no negative eigenvalues, while the saddle points corresponding to the transition structures each have one. The optimized geometries and relative energies are shown in Figure 1. Full geometries are given in Table I.

## Results and Discussion

The reaction of formaldehyde with allylborane proceeds first by the formation of an allylborane–aldehyde complex, **2**. The conversion of this complex to the addition product is highly exothermic (−44 kcal/mol) and has an early transition structure with a very small reaction barrier (1.8 kcal/mol via **TS1**) relative to the borane–aldehyde complex.[9] Complex **2**, which is 17 kcal/mol more stable than the reactants,[10] was located by beginning with the transition structure geometry (**TS1**) and gradually

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(8) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

(9) Allylboration of aldehydes with allylboranes occurs at −50 °C to 20 °C and generally is complete within a few minutes.

(10) Experimentally, the complexation of triallylborane with pyridine and other amines is exothermic by 20–25 kcal/mol, but coordination with tetrahydrofuran is weaker, see ref (6a).

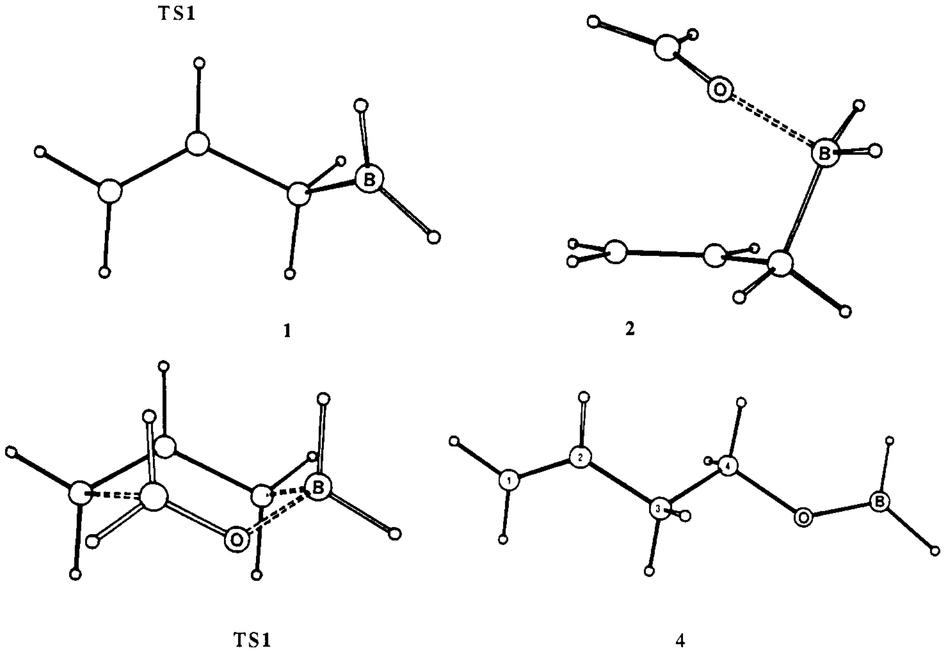
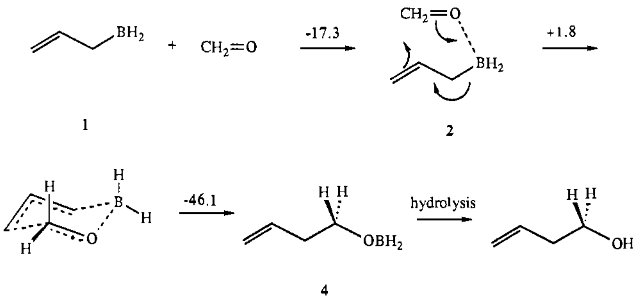


**Figure 1.** The 3-21G intermediates and transition structures and relative energies (kcal/mol) for the reaction of allylborane with formaldehyde.

lengthening the distance between two carbon atoms of the reaction center, followed by full optimization. Several conformers of the complex were also optimized but were found to have higher energy than **2**. The distance between the reacting carbons in the complex is 3.05 Å, which is somewhat less than the sum of van der Waals radii of two $sp^2$ carbons. Even in the complex, there may be small attractive interactions between the $sp^2$ carbon termini of the reactants. In the transition structure, this length decreases to 2.3 Å.



The chair and twist-boat transition structures are shown in Figure 2. The chair transition structure (**TS1**) clearly resembles a cyclohexane chair conformation, with a forming C–C bond length of 2.27 Å and other skeletal bond lengths distorted only about 10–30% away from those found for the reactant complex. The geometry of the allyl fragment in the transition structure is anti-bent about both of the partially formed C–C double bonds, similar to the transition structure geometry postulated for $S_N2'$ reactions.[11] The central carbon of the allyl group is significantly pyramidalized: it is distorted about 15% from a planar $sp^2$ carbon to a tetrahedral $sp^3$ carbon, which corresponds to an out-of-plane bending angle of 3°. The torsional angle around the forming C–C bond (O–C—C–C) is 54°, which is very close to that of a perfectly staggered conformation and is about the same as the 55° torsional angle of cyclohexane. The boron is coordinated with an in-plane lone-pair on oxygen in both the complex and in the chair transition structure.

There are three conceivable boat transition structures, in which various cross-ring groups are located in the bow and stern positions. We were able to locate only one of them and could not find any evidence for the existence of others. The twist-boat transition structure which was located has the carbonyl oxygen and the central allyl carbon at the bow and stern. Transition structure **TS2** is 8.3 kcal/mol higher in energy than the chair transition structure at the 3-21G level. The calculated preference for a chair conformation over a boat is higher than the estimate of ~3 kcal/mol based upon the stereochemistry of the analogous Claisen rearrangement.[3a] Experimental studies indicate that the chair transition state of the Claisen rearrangement is favored by ~3 kcal/mol relative to the boat, while ab initio calculations indicate a 5–6 kcal/mol preference.[12]

It has been shown that predictions of relative energies of conformations can be improved by using the 6-31G* basis set. Therefore, we carried out single point calculations with the 6-31G* basis set based upon the geometries optimized at the 3-21G level. The twist-boat transition structure is 8.9 kcal/mol higher in energy than the chair at the 6-31G* level. The calculated value is also larger than the energy difference between the corresponding conformations of tetrahydropyran.[13] Therefore, steric interactions of the eclipsing groups in the twist-boat transition structure may not account for all the disfavorable effects in the twist-boat transition structure. Presumably, interactions between the frontier orbitals on the allyl-CH carbon and the aldehyde oxygen atom also disfavor the boat transition structure. Indeed, the Mulliken population analysis of the transition structures shows that substantial repulsive interactions between the oxygen and the allyl-CH carbon exist in the twist-boat transition structure. Since the twist-boat is so unfavorable, it is likely that the minor stereoisomer observed in experimental allylborations arises from unfavorable conformations of the chair transition state.

Both chair and twist-boat transition structures were located for the reaction of formaldehyde with allylboronic acid at the 3-21G level. The allylboronic acid was used as a model for the cyclic allylboronic esters commonly used in synthesis. We had to constrain the H–O–B–O(H) dihedral angle to be 0° during the optimization in order to avoid hydrogen bonding of the OH groups on the boron with the carbonyl oxygen. This geometry mimics that of the cyclic boronate. The chair transition structure is 8.2 kcal/mol more stable than the twist-boat. The chair and twist-boat transition structures for the reactions of allylboronic acid occur

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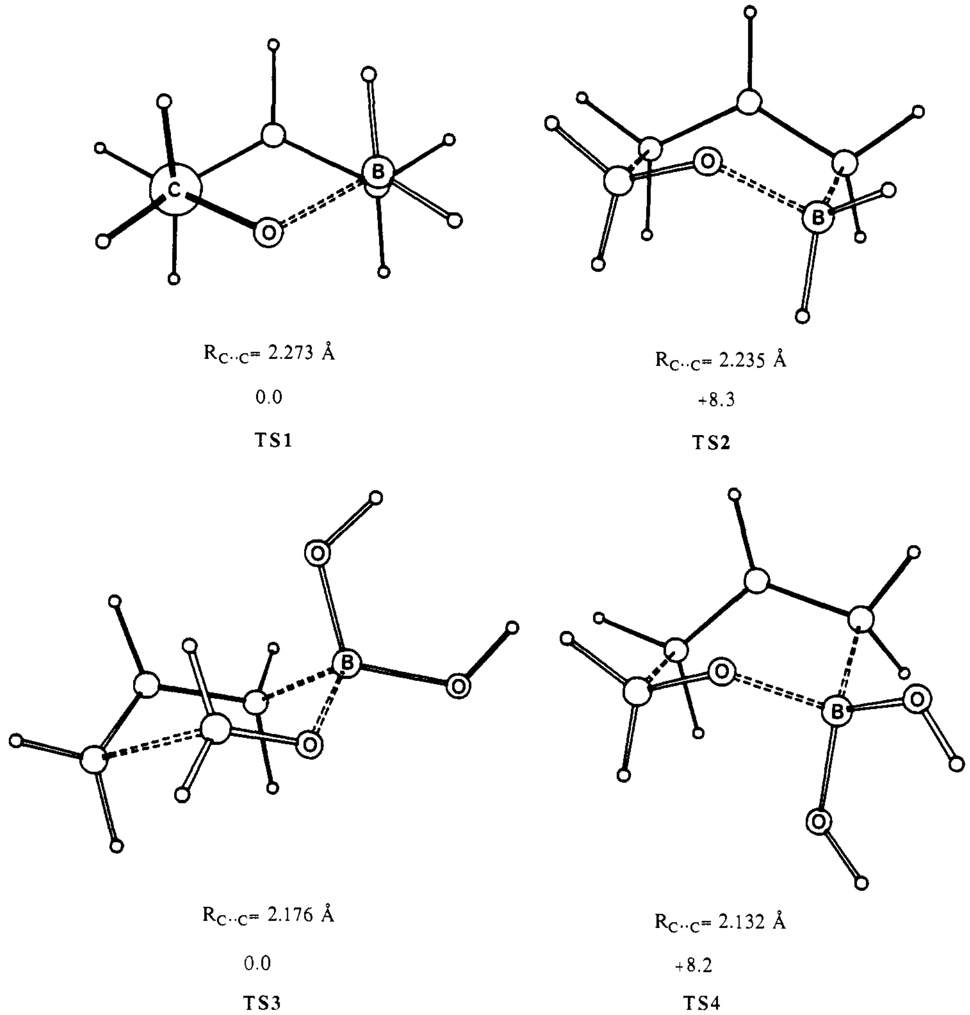


$R_{C\cdots C}$= 2.273 Å
0.0
TS1

$R_{C\cdots C}$= 2.235 Å
+8.3
TS2

$R_{C\cdots C}$= 2.176 Å
0.0
TS3

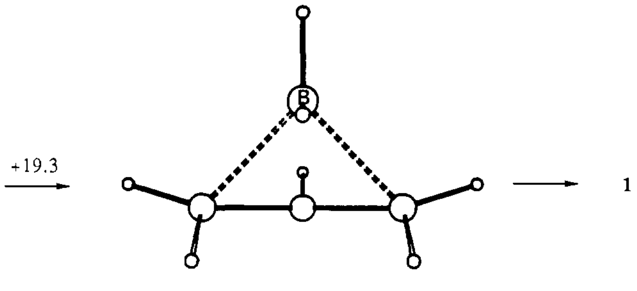
$R_{C\cdots C}$= 2.132 Å
+8.2
TS4

**Figure 2.** The 3-21G chair and boat transition structures and relative energies (kcal/mol) for the reaction of formaldehyde with allylborane and allylboronic acid.

later along the reaction coordinate as compared to those of allylborane. As shown in Figure 2, the forming C–C bond lengths are about 0.1 Å shorter in transition structures of allylboronic acid than those of allylborane, while other bond lengths change less than 0.04 Å. In the chair transition structure, the axial O–B bond length is longer than the equatorial one by 0.03 Å, indicating that anomeric effects may exist in the transition structure.

Given a chair transition structure, the relative energies of axial and equatorial conformations of alkyl groups were assessed computationally by replacing the appropriate hydrogen with a standard methyl group ($R_{CC}$ = 1.54 Å, $R_{CH}$ = 1.08 Å, ∠CCH = 109.5°). Single point calculations at the 3-21G level indicate that a methyl group attached to carbonyl carbon prefers the equatorial position over the axial by 5.5 kcal/mol. Similarly, a methyl group α to boron prefers the equatorial position by 2.4 kcal/mol. Single point calculations also predict that fluorine atom at the carbon α to boron prefers the axial position over the equatorial position by 3.5 kcal/mol. Although the calculated preferences are likely too high, they are consistent qualitatively with the experimental observations that α-alkyl-substituted allylborane gives *trans*-olefin product, while *cis*-olefin products are obtained for halogen and alkoxy substituents at the α carbon.[14]

A related reaction in allylborane chemistry, which can interfere with the regioselectivity of the allyl transfer reaction, is the intramolecular allylic rearrangement. Triallylborane undergoes rearrangement readily with an activation energy of approximately 10 kcal/mol.[6] PRDDO calculations predict a barrier of 11 kcal/mol for the **1**,3-boron shift of allylborane.[15] For the 1,3-shift of allylborane, the transition structure was located by constraining the $BH_2$ group symmetrically and optimizing this structure to a local minimum. The optimized local minimum is indeed the transition structure for the 1,3-shift of allylborane as characterized by vibrational frequency calculations. The transition structure of the rearrangement is shown in Figure 3. Our calculations indicate the barrier of this rearrangement is 19 kcal/mol at the RHF level with the 3-21G basis set. When correlation correction is included, the barrier drops to a more realistic value of 7.3 kcal/mol at the MP2/3-21G level based upon the RHF geome-



TS5

**Figure 3.** The 3-21G transition structure of the 1,3-sigmatropic $BH_2$ shift of allylborane.

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tries. The barrier of 1,3-boron shift is expected to be higher in ether solvent because of dissociation of boron–ether coordination in the transition state.

## Conclusion

Ab initio molecular orbital calculations predict that chair transition structures are preferred for the reaction of formaldehyde with allylborane and allylboronic acid. The transition structures found here should be good models for the transition structure of reactions of allyl(dialkyl)borane and allylboronate reactions with carbonyl compounds. Development of a force field to treat stereoselectivity of highly substituted cases efficiently and quantitatively will be reported at a later date.

**Acknowledgment.** We thank Dr. David C. Spellmeyer for helpful assistance with the computations, Professor R. W. Hoffmann for helpful and stimulating discussions, and the National Institutes of Health for financial support of this research.

**Registry No. 1**, 51531-21-6; HCHO, 50-00-0; allylboronic acid, 88982-39-2.

**Supplementary Material Available:** Energies (au) and internal coordinates (lengths in Å, angles and dihedral angles in deg) of the stationary points for the reaction of formaldehyde with allylborane and allylboronic acid and the rearrangement of allylborane (23 pages). Ordering information is given on any current masthead page.

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# The Angular Dependence of Geminal Deuterium Isotope Effects on $^{13}$C NMR Spectra in Carbonyl Compounds

**Stefan Berger* and Bernd W. K. Diehl**

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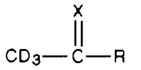
**Abstract:** The measurement of intrinsic deuterium isotope effects over two bonds in carbonyl compounds reveals a dependence of the dihedral angle between the direction of the $\pi$-orbital of the carbonyl group and the direction of the C–D $\sigma$-bond. This angular dependence is superimposed on a general dependence between deuterium isotope effects and the chemical shift. The results are discussed in terms of hyperconjugation. Applications of these findings for conformational analysis are shown.

The study of intrinsic deuterium isotope effects on $^{13}$C NMR spectra can be of importance in understanding the behavior of the $^{13}$C chemical shift.[1,2] The small perturbations caused by the isotope often reflect on a minor scale the action of substituents.[3,4] Because of the vibrational origin,[2] the isotope effects over one or two bonds should be all negative.[5] This implies that in deuterated compounds the carbon atoms are shielded compared with the parent compounds; this is expected owing to the shorter C–D distance caused by a lower zero-point vibration in an asymmetric potential.[2] Exceptions have long been known, however, and a positive isotope effect at the carbonyl carbon atom, for example, in deuterated acetone was reported very early.[8] This was recently remeasured and compared with the tritiated compound.[9] In fact, there is a correlation between $^{13}$C NMR chemical shifts and the deuterium isotope effect over two bonds ($^2\Delta$) in $\alpha$-deuterated compounds of type I, spanning a chemical shift range of 150 ppm and deuterium isotope effects between +200 and −200 ppb.[10] A similar relationship was recently published for cations.[11] We had independently found[12] that such a relationship exists not only for sp$^2$-hybridized carbon atoms but is valid for the complete range of $^{13}$C NMR chemical shifts, although exceptions are known.[11] An example is given for some bicyclic compounds in Figure 1. Thus a connection between deuterium isotope effects and chemical shifts of the carbon atoms seems to be more general. We maintained earlier that deuterium isotope effects display on a minor scale the behavior of normal substituents.[13] Therefore, it was tempting to plot substituent-induced shifts versus chemical shifts of the relevant carbon atoms. In Figure 2 the results for the substituent-induced shift of a bromine atom at a $\beta$-carbon atom is shown which displays an obvious linear relationship. Preliminary data analysis shows that a relationship as plotted in Figure 2 could possibly be more general.[14]



$$CD_3{-}\overset{\overset{\textstyle X}{\|}}{C}{-}R$$

I

X = =O, =CR$_2$, =NH

R = O, C, Hal, H

This explains, for instance, why $^{13}$C NMR increment systems only work well for a narrow group of compounds, e.g., substituted benzenes, since the chemical shifts in such a group are all rather similar. A chemical shift dependence of substituent effects could be the underlying reason for the nonadditivity of chemical shifts in para-disubstituted aromatic compounds.[15]

Remarkable in Figure 2 is the sign change of substituent effects. This was found for the geminal isotope effects as well by us and by Arrowsmith and Kresge.[10] Positive and negative isotope effects, however, require, according to these authors, at least two mech-

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(5) There is considerable confusion about the sign convention of deuterium isotope effects. When we started in this field, we adopted negative signs for upfield deuterium isotope effects.[6] Guided by referees of different journals and in congruence with the leading review articles,[1] we changed the signs in our subsequent papers.[3,4,7] After submission of this paper both referees preferred the other sign. Since in this paper it is shown that deuterium isotope effects behave similarly to substituent effects, we are happy to return to our original sign convention.

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