

New Computational and Experimental Evidence for the Mechanism of the Sakurai Reaction

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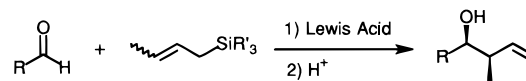
Abstract: Reaction of aldehydes with allyltrimethylsilane promoted by BF₃ (Sakurai reaction) affords fluorotrimethylsilane and a borylated homoallylic alcohol in a noncatalytic fashion. These reaction products have been identified through ¹³C NMR and ²⁹Si NMR. A model system formed by acetaldehyde, allylsilane, and BH₂F has been used to investigate the mechanism of this reaction at the DFT computational level. Four transition states, quite close in energy, have been found for the model reaction. These transition states, which explain the stereochemical features of the Sakurai reaction, correspond to eight-membered cyclic structures deriving from C–C (tight) and Si–F (loosen) bond formation and synclinal (gauche) disposition of the reacting double bonds. No antiperiplanar or six-membered cyclic transition structures have been located.

Introduction

The mechanism of the addition reactions to aldehydes of allylic nucleophiles promoted by Lewis acids¹ has been the object of a long-lasting debate in the community of organic chemists, since the discovery of the *syn*-convergent diastereoselectivity of the allylsilane addition (Sakurai reaction, Scheme 1)^{2,3} and allylstannane addition.⁴ Classic chair-like "cyclic" transition states⁵ cannot easily account for the observed stereochemistry, and "open" transition state models have been generally adopted. However, many questions concerning the mechanism of these reactions remain unclear.

In acyclic systems Kumada et al. showed that the addition of allylsilanes to aldehydes promoted by TiCl₄ follows an *anti*-S_{E'} mechanism^{6a,b} (antarafacial orientation of the trialkylsilyl group and the incoming aldehyde), although other kinds of

Scheme 1. The Sakurai Reaction



electrophiles behave in the opposite way.^{6c} The same result was unambiguously obtained by Denmark using a cyclic bifunctional probe.⁷ In these reactions the *anti*-S_{E'} mechanism prevents the occurrence of six-membered cyclic transition states (*trans*-cyclohexene type structure). However, the rigidity of Denmark's probe does not allow the testing of all the possible orientations of the reagents, while Kumada's model is strongly sterically biased.

Open transition state models offer complete freedom to the relative orientation of the reagents. Among the various possibilities, the antiperiplanar (*anti* orientation of the reacting C=C and C=O bonds) arrangement provides a straightforward explanation of the *syn* selectivity of the allylation reaction. It was originally introduced by Yamamoto^{4,8} to account for the results obtained with crotylstannanes; later on this model was applied to allylsilanes.² However, a substantial crop of stereochemical findings, obtained for both reagents, shows a better fit with a synclinal model.⁹

Since the interest for the Sakurai and related reactions has greatly grown up in the last years with the development of efficient catalytic asymmetric methodologies used to carry out these reactions,¹⁰ we have decided to perform a combined experimental and computational study of the mechanism of the Sakurai reaction. We wish to emphasize that, to our knowledge, our work represents the first determination of the structure of

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(1) For reviews on the aldehyde allylation see: (a) Fleming, I. *Org. React.* **1989**, *37*, 57. (b) Fleming, I. In *Comprehensive Organic Synthesis*; Heathcock, C. H., Ed.; Pergamon Press: Oxford, 1991; Vol. 2, p 563. (c) Sakurai H. *Pure Appl. Chem.* **1992**, *54*, 1. (d) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207. (e) Nishigaichi, Y.; Takuwa, A.; Naruta, Y.; Maruyama, K. *Tetrahedron* **1993**, *49*, 7395. (f) Masse, C. E.; Panek, J. S. *Chem. Rev.* **1995**, *95*, 1293.

(2) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, *16*, 1295.

(3) Hayashi, T.; Kabeta, K.; Hamachi, I.; Kumada, M. *Tetrahedron Lett.* **1983**, *24*, 2865.

(4) Yamamoto, Y.; Maruyama, K.; Naruta, Y.; Yatagai, H. *J. Am. Chem. Soc.* **1980**, *102*, 7101.

(5) Cyclic transition states have been proposed for the reactions of allylsilacyclobutanes (Matsumoto, K.; Oshima, K.; Utimoto, K. *J. Org. Chem.* **1994**, *59*, 7152) and allyltrifluorosilanes (Kobayashi, S.; Nishio, K. *J. Org. Chem.* **1994**, *59*, 6620). These transition structures have recently been determined with theoretical methods: Fujimoto, H.; Omoto, K.; Sawada, Y. *J. Am. Chem. Soc.* **1996**, *118*, 1750–1755. Also the thermal or pressurized reaction of allylstannanes with aldehydes has been proposed to proceed through cyclic transition states: Yamamoto, Y.; Maruyama, K.; Matsumoto, K. *J. Chem. Soc., Chem. Commun.* **1983**, 489. A theoretical investigation of the allylation with allyl tetrafluorosilicates has shown that this reaction involves a cyclic transition structure: Kira, M.; Sato, K.; Sakurai, H.; Hada, M.; Izawa, M.; Ushio, J. *Chem. Lett.* **1991**, 387.

(6) (a) Hayashi, T.; Konishi, M.; Ito, H.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4962. (b) Hayashi, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4963. (c) Wetter, H.; Scherer, P.; Schweizer, W. B. *Helv. Chim. Acta* **1979**, *62*, 1985.

(7) Denmark, S. E.; Almstead, N. G. *J. Org. Chem.* **1994**, *59*, 5130.

(8) Yamamoto, Y.; Yatagai, H.; Ishihara, Y.; Maeda, N.; Maruyama, K. *Tetrahedron* **1984**, *40*, 2239–2246.

(9) Allylsilanes: (a) Denmark, S. E.; Weber, E. J. *Helv. Chim. Acta* **1983**, *66*, 1655. (b) Denmark, S. E.; Weber, E. J.; Wilson, T. M.; *Tetrahedron* **1989**, *45*, 1053. (c) Mikami, K.; Maeda, T.; Kishi, N.; Nakai, T. *Tetrahedron Lett.* **1984**, *25*, 5151. Allylstannanes: (d) Denmark, S. E.; Hosoi, S. *J. Org. Chem.* **1994**, *59*, 5133. (e) Keck, G. E.; Dougherty, S. M.; Savin, K. A. *J. Am. Chem. Soc.* **1995**, *117*, 6210–6223. (f) Gevorgyan, V.; Kadota, I.; Yamamoto, Y. *Tetrahedron Lett.* **1993**, *34*, 1313. See also: Fleming, I. *Chemtracts* **1991**, *4*, 21.

Scheme 2

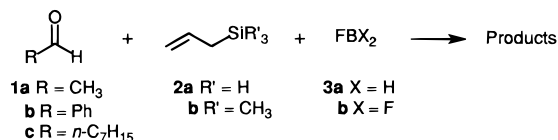


Table 1. Reaction of Aldehydes with Allyltrimethylsilane Promoted by BF₃·OEt₂^a

aldehyde	3b (equiv)	<i>T</i> (°C)	<i>t</i> (min)	conv, % ^b	products, (yield %) ^b
1b	0.2	-80→RT	240 ^c	20	4b (8), 7b (12)
1b	1	-80	120	60	4b (24), 7b (36)
1b	1	RT	1	50	4b (32), 7b (18)
1c	0.2	-80→RT	240 ^c	30	4c (17)
1c	1	-80	240	100	4c (73)
1c^d	1	RT	60	100	4c (47)

^a All reactions were carried out with a 1:2 = 1.0:1.0 molar ratio in CH₂Cl₂ and quenched with pH 7 aqueous buffer solution. ^b Determined gas chromatographically. ^c Longer reaction times did not afford significant change in the composition of the reaction mixture. ^d The reaction was carried out in pentane.

the transition state of a Lewis acid-promoted addition of carbon nucleophiles to carbonyl compounds. Our results, besides clarifying the mechanism of the reaction between allylsilanes and aldehydes, can be a useful tool for understanding related processes such as the allylstannane addition and the silylenol ether addition (Mukaiyama reaction¹¹).

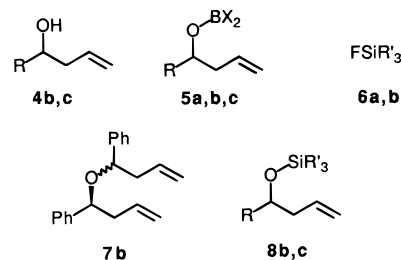
Results and Discussion

In this work we have experimentally investigated the Sakurai reaction involving benzaldehyde (**1b**) or octanal (**1c**), allyltrimethylsilane (**2b**), and BF₃·OEt₂ (**3b**) (Scheme 2). In our computations we have considered the model reaction between acetaldehyde (**1a**), allylsilane (**2a**), and BH₂F (**3a**).

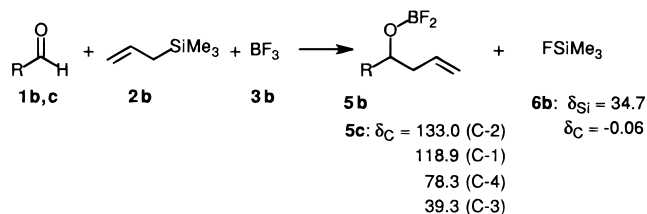
Experimental Findings. We have carried out the experimental reactions in CH₂Cl₂ and pentane using **1b** and **1c** under both stoichiometric and catalytic conditions (1.0 or 0.2 mol equiv of **3b**). We have found that the conversion of the aldehyde has never exceeded the amount of the Lewis acid employed (Table 1).

As expected, the common products of the two reactions, after quenching with water, are the homoallylic alcohols **4b,c** (Chart 1). However, the two substrates differ in the byproducts afforded: the diastereomeric ethers **7b** are provided by benzaldehyde in substantial amount, while only minor quantities of a complex mixture of byproducts are obtained from octanal. The bis-homoallylic hydrocarbon product, which was found by Mayr and Gorath¹² in a recent study on the same reaction, could not be detected in our reaction mixtures. In all cases no traces of the homoallylic silyl ethers **8b,c** have been observed.

Chart 1. Reaction Products [**a**: R = CH₃, R' = H, X = H (Computational); **b**: R = Ph, R' = CH₃, X = F (Experimental); **c**: R = *n*-C₇H₁₅, R' = CH₃, X = F (Experimental)]



Scheme 3



Investigation by ²⁹Si NMR has demonstrated that fluorotrimethylsilane (**6b**) (δ_{Si} : 34.7 ppm, $J_{Si-F} = 273$ Hz) is the only silylated product formed in the temperature range from -80 to 20 °C in the reactions of **1b** or **1c** with **2b** + **3b**. This finding is in agreement with the production of ClSiMe₃ found by Retz^{13a} and Denmark^{13b} in the corresponding reactions promoted by TiCl₄. The detection of **5** has been less straightforward, since reference spectra are unavailable. Nevertheless, ¹³C-NMR investigation of the reaction mixture of **1c** + **2b** + **3b** in CH₂Cl₂ showed the presence of **6b** ($\delta_C = 0.06$ ppm, $J_{C-F} = 14.9$ Hz) and of a new allylic product with a characteristic set of signals: $\delta_C = 133.0$ (C-2), 118.9 (C-1), 78.3 (C-4), 39.3 (C-3) ppm; the same product has been found to form in the treatment of either the alcohol **4c** or the silylether **8c** with BF₃·OEt₂; on this basis we attribute this set of signals to **5c**.¹⁴ In all cases, upon quenching with water, these reactions afforded **4c** as the sole or major product. Since the desilylation of **8c** by BF₃·OEt₂ is very fast, we cannot rule out the transient formation of a silylated product **8**, which eventually undergoes exchange with BF₃, but the available experimental data support the hypothesis of a direct formation of the borylated homoallylic alcohol **5b,c** and of **6b** from the reaction of aldehydes and allylsilanes in the presence of BF₃ (Scheme 3).

Computational Findings. The model reaction **1a** + **2a** + **3a** has been investigated at the density functional theory (DFT)¹⁵ level with use of the Gaussian 94¹⁶ series of programs. The

(13) (a) Retz, M. T.; Raguse, B.; Marth, C. F.; Hugel, H. M.; Bach, T.; Fox, D. N. A. *Tetrahedron* **1992**, *48*, 5731. (b) Denmark, S. E.; Almstead, N. G.; *Tetrahedron* **1992**, *48*, 5565.

(14) Also a different allylic product **5'c** having $\delta_C = 135.3$ (C-2), 117.5 (C-1), 73.2 (C-4), 41.5 (C-3) ppm formed in minor amount from either the allylation reaction or the desilylation of **8c** with BF₃·OEt₂. In the latter case the relative amount of **5c** and **5'c** was found to vary depending on the relative amount of the reagents; on this basis we tentatively attribute an (RO)₂BF structure to **5'c**.

(15) Parr, R. G.; Yang W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New-York, 1989.

(16) Gaussian 94, Revision D.3, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; and Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995.

(10) Allylstannanes: (a) Costa, A. L.; Piazza, M. G.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Am. Chem. Soc.* **1993**, *115*, 7001. (b) Keck, G. E.; Tarbet, K. H.; Geraci, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 8467. (c) Keck, G. E.; Krishnamurthy, D.; Grier, M. C. *J. Org. Chem.* **1993**, *58*, 6543. (d) Weigand, S.; Brukner, R. *Chem. Eur. J.* **1996**, *2*, 1072. (e) Bedeschi, P.; Casolari, S.; Costa, A. L.; Tagliavini, E.; Umani-Ronchi, A. *Tetrahedron Lett.* **1995**, *36*, 7897. (f) Yanagisawa, A.; Nakashima, H.; Ishiba, A.; Yamamoto, H. *J. Am. Chem. Soc.* **1996**, *118*, 4723. (g) Yanagisawa, A.; Ishiba, A.; Nakashima, H.; Yamamoto, H. *Synlett* **1997**, 88. Allylsilanes: (h) Hishihara, K.; Mouri, M.; Gao, Q.; Maruyama, T.; Furuta, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 11490. (i) Carreira, E. M.; Gauthier, D. R., Jr. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2363.

(11) Mukaiyama, T.; Banno, K.; Narasaka, K. *J. Am. Chem. Soc.* **1974**, *96*, 7503. See also: Gennari, C. In *Comprehensive Organic Synthesis*; Trost, B. M., Flemings, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 2, p 629.

(12) Mayr, H.; Gorath, G. *J. Am. Chem. Soc.* **1995**, *117*, 7862.

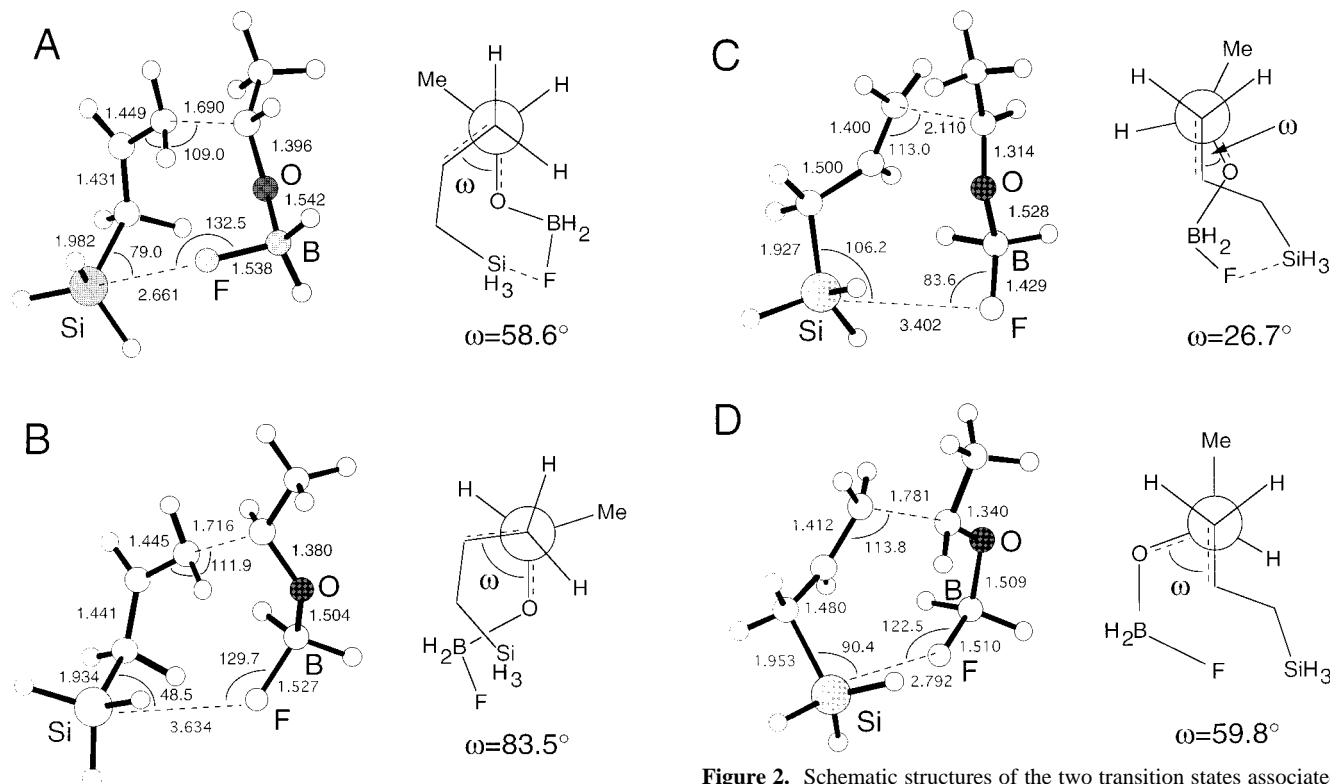


Figure 1. Schematic structures of the two transition states associated with an *anti*- S_E' attack of the electrophile (bond lengths are in angstroms and angles in degrees).

nonlocal hybrid three-parameter functional proposed by Becke¹⁷ (B3LYP) and available in Gaussian 94 has been used. A DZ Dunning basis set^{18a} including *sp* diffuse functions^{18b} on oxygen ($\xi = 0.00845$), boron ($\xi = 0.00315$), and fluorine ($\xi = 0.01076$) and *d* orbitals on silicon ($\xi = 0.3247$) has been used. The geometries have been fully optimized with the gradient method. The vibrational frequencies and the intrinsic reaction path (IRC)¹⁹ have been calculated at the same level of theory.

Four transition structures **A**, **B**, **C**, and **D** have been located on the potential energy surface. These structures are schematically represented in Figure 1 (**A** and **B**) and Figure 2 (**C** and **D**) together with the values of the most relevant geometrical parameters. We must point out that (i) since any significant Si–O interaction is lacking, all these structures apparently correspond to “open” transition states and that (ii) *in spite of extensive search no six-membered “cyclic” transition structures have been found*. However, a deeper inspection of the structures reported in the figures shows that the silicon and the fluorine atoms are not too far away: the Si–F distance ranges from 2.661 Å in **A** to 3.634 Å in **B**. These distances are probably associated with an electrostatic interaction between the two atoms (the net charges on Si and F in structure **A** are 0.36 and –0.40, respectively) and suggest, especially in **A** and **D**, an incipient Si–F bond. Consequently they could be considered eight-membered cyclic structures:²⁰ structure **A** resembles the boat-boat (BB) conformation of cyclooctane and **C** corresponds

Figure 2. Schematic structures of the two transition states associated with a *syn*- S_E' attack of the electrophile (bond lengths are in angstroms and angles in degrees).

to a highly distorted chair-chair (CC) conformation of cyclooctane while a sort of boat-chair (BC) and boat-half-chair (BHC) conformation can be recognized in structures **B** and **D**, respectively.²¹ All these structures are characterized by a synclinal arrangement of the reacting C=O and C=C double bonds (the dihedral angle ω is 58.6° in **A**, 83.5° in **B**, 26.7° in **C**, and 59.8° in **D**). In spite of accurate investigation of the potential energy surface no *antiperiplanar transition structures* (dihedral angle ω close to 180°) have been located. Even if the Si–F incipient bond is quite loose, nevertheless this interaction seems to be crucial in determining the reaction path toward the products: *analysis of the reaction coordinate in the product direction by computing the intrinsic reaction path (IRC) shows that the Si–F distance decreases (formation of a new Si–F bond) and the Si–C and B–F distances increase (breaking of the two corresponding bonds) to afford 5a and 6a, which correspond to the experimentally observed products*. From this point of view the proposed mechanism appears to be related to the push–pull hypothesis of Yamamoto,^{1d,9f} who says that both acidic activation of the carbonyl and contemporary nucleophilic attack to tin (or silicon) are essential for the accomplishment of the allylation reaction.

Two of the four TS's, namely the BB structure **A** and the BC structure **B**, derive from an *anti*- S_E' attack of the electrophile on the allylsilane, while **C** and **D** correspond to a *syn*- S_E' approach. Since **A** and **B** are diastereotopic (the opposite faces of the prochiral aldehyde are involved in the reaction) they would lead to opposite stereoisomers if 3-substituted allylsilanes were in use; the same considerations hold for **C** and **D**.

The energy values for the four transition structures and the products are collected in Table 2. The relative energy values, computed with respect to reactants, approximately correspond to the activation energies for the four reaction channels and to the reaction enthalpy. From the values reported in Table 2 it

(21) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley: New York, 1994.

(17) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(18) (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1970**, *53*, 2823. (b) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comp. Chem.* **1993**, *4*, 294.

(19) (a) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363. (b) Gonzales, C.; Schlegel, H. B. *J. Chem. Phys.* **1991**, *95*, 5853.

(20) A hypothetical 8-membered transition state has been quite recently proposed as a rationale for the catalytic asymmetric Sakurai reaction developed by Carreira.¹⁰ⁱ Duthaler, R. O.; Hafner, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 43.

Table 2. Absolute (E)^a and Relative (ΔE)^b Energies of Reactants and Transition States for the Model Reaction **1a** + **2a** + **3a** Computed at the B3LYP and MP2 Levels

	B3LYP		MP2	
	E	ΔE	E	ΔE
reactants	-688.34948	0.00	-686.12382	0.00
A	-688.33668	8.03	-686.10793	9.97
B	-688.33118	11.48	-686.09318	19.23
C	-688.33144	11.32	-686.10136	14.09
D	-688.33813	7.12	-686.10733	10.35
products	-688.40494	-34.80	-686.18666	-39.43

^a Hartrees. ^b kcal mol⁻¹.

is evident that the reaction is quite exothermic (-34.80 kcal mol⁻¹). Furthermore, structures **A** and **D** have the lowest activation energies (8.03 and 7.12 kcal mol⁻¹, respectively) while **B** and **C** are higher in energy and are almost degenerate (11.48 and 11.32 kcal mol⁻¹, respectively). In the same table we have also reported the energy values obtained at the MP2 level on the B3LYP optimized geometries. At the MP2 level the reaction is still highly exothermic (-39.43 kcal mol⁻¹); even if the energetic order of the four transition states remains approximately the same (**A** and **D** are still characterized by the lowest activation energies: 9.97 and 10.35 kcal mol⁻¹ respectively), the activation energy of **B** becomes much larger (19.23 kcal mol⁻¹). However, these values should be considered with great care since no geometry optimization was performed at the MP2 level.

It is reasonable to believe that the energetic order of the four structures **A**, **B**, **C**, and **D** can change significantly when hydrogens on allylsilane are substituted with larger groups. In particular a critical interaction should occur in the real systems between the trimethyl(or larger)silyl group SiR₃ and the fluorine atoms of the Lewis acid. This interaction should rise the energy of both structures **C** and **D** with respect to **A** and **B** because of the *syn* orientation of the silyl group, which makes it more difficult to accommodate cumbersome substituents on the Si atom. It is interesting to point out that the most likely geometry transformation that can minimize the repulsions in **C** and **D** is a rotation around the C-C single bond of allylsilane to reach an *anti* orientation of SiR₃. On the contrary, in **A** and **B** a further rotation around the C-C bond can lower the repulsive interactions but leaves unchanged the *anti* orientation of the silyl group. This hypothetical behavior can be a rationale for the *anti* preference found by Kumada^{6a} and Denmark.⁷ The two *anti*-S_E' diastereotopic transition states **A** and **B**, which would be associated to the most likely reaction channels in real systems, easily explain the *syn* diastereoconvergence of the Sakurai reaction: if the reaction proceeds through transition state **A** the *syn*- or *anti*-homoallylic alcohols can be obtained from the (*E*)- or (*Z*)-crotylsilane, respectively. On the contrary, if transition state **B** is involved, the *syn* or *anti* products are obtained from the *Z*- or *E*-isomer, respectively. Thus the stereochemical outcome of the reaction could depend on the relative energy of **A** and **B**, which will be determined by the nature of substituents in real systems.²²

Conclusions

In this paper we have studied from both computational and experimental points of view the mechanism of the Sakurai reaction. Even if we cannot completely rule out that other more

accurate theoretical methods can give qualitatively different results, we believe that our finding can shed light on the mechanism of this important reaction. In particular we have found that (i) no six-membered cyclic or antiperiplanar transition states exist on the reaction surface (ii) the addition of allylsilane on a BF₃-complexed aldehyde occurs through eight-membered cyclic transition states with synclinal arrangement of the reacting C=C and C=O double bonds. The formation of the new C-C and Si-F bonds and the breaking of the Si-C and B-F bonds occur in a highly asynchronous, concerted manner and lead to the fluorosilane **6** and the homoallylborate **5** experimentally observed. These products represent the thermodynamically most favorable state of the system; thus, the lack in regeneration of the Lewis acid prevents the catalysis.

Even if four transition states have been located on the reaction surface, we suggest that, in the real experimental conditions, the two most likely reaction channels are those involving the *anti*-S_E' diastereotopic transition states **A** and **B** where the repulsive interaction between the trialkylsilyl group and the fluorine atoms of the Lewis acid can be minimized. These two transition states, whose relative stability appears to be determined by the nature and position of the substituents, easily explain the stereochemical features experimentally observed for this reaction

Experimental Section

¹H NMR, ¹³C NMR, and ²⁹Si NMR spectra were obtained with a Varian Gemini-300 instrument at 300, 75.5, and 59.6 MHz, respectively, and are reported in δ units, referenced to TMS (internal standard). IR spectra were recorded with a Nicolet 205 FT instrument and are reported in cm⁻¹. MS spectra were obtained with the GC-MS technique on a Hewlett-Packard 5890 analyzer with EI at 70 eV and are given as *m/e* (rel intensity). All the reactions were carried out under Ar atmosphere in anhydrous pentane (Na) or CH₂Cl₂ (CaH₂). Aldehydes were distilled prior to use; other chemicals were used as received (98% pure or better).

Allylation of Benzaldehyde. A solution of **1b** (0.102 mL, 1 mmol) and **3b** (0.127 mL, 1 mmol; or 0.025 mL, 0.2 mmol) in anhydrous CH₂Cl₂ was cooled at the desired temperature (Table 1). After 10 min, **2b** (0.160 mL, 1 mmol) was added with stirring. When the time reported in Table 1 was passed, the reaction was quenched with Na₂HPO₄/NaH₂PO₄ aqueous buffer solution (pH 7, 3 mL), extracted with ether, and dried (Na₂SO₄). The products obtained were purified by silica gel chromatography.

Allylation of Octanal. Premixing of **1c** and **3b** caused the formation of a complex scarcely soluble in either CH₂Cl₂ or pentane; therefore inverse addition was adopted. A solution of **1c** (0.156 mL, 1 mmol) and **2b** (0.160 mL, 1 mmol) in CH₂Cl₂ or pentane (3 mL) was cooled at the desired temperature (Table 1). Then **3b** (0.127 mL, 1 mmol; or 0.025 mL, 0.2 mmol) was added with stirring. Quenching and workup procedures were the same as for **1a**.

α -(2-Propen-1-yl)benzenemethanol (4b**) and 1-undecen-4-ol (**4c**)** showed identical spectroscopic properties to those previously reported.^{10a}

Ethers 7b. First isomer: MS 237 (15), 195 (2), 131 (100), 116 (41), 91 (99), 77 (45). IR 3078, 3029, 2980, 2931, 2910, 1664, 1602, 1489, 1454, 1363, 1307, 1082, 990, 913, 765, 702. ¹H NMR 2.38-2.62 (m, 4H), 4.10 (t, 2H, *J* = 6.3 Hz), 4.95 (m, 4H), 5.60 (m, 2H), 7.25 (m, 10H). ¹³C NMR 42.8, 77.4, 116.6, 126.7, 127.5, 127.9, 134.9, 142.0. **Second isomer:** ¹H NMR 2.22-2.35 (m, 4H), 4.40 (t, 2H, *J* = 6.3 Hz), 4.90-5.10 (m, 4H), 5.80 (m, 2H), 7.25 (m, 10H). ¹³C NMR 41.6, 77.0, 117.0, 127.1, 128.0, 128.2, 134.7, 142.0.

Spectroscopic Investigations. For ²⁹Si NMR and ¹³C NMR investigations the reaction mixture of **1b** or **1c**, **2b**, and **3b** was prepared in an NMR tube under Ar atmosphere at -80 °C in anhydrous CH₂Cl₂, containing 10% C₆D₆ for the lock, immediately before use, and quickly transferred into the NMR instrument set at the desired temperature. Recording of ²⁹Si NMR spectra showed the signals of allyltrimethylsilane (**2b**) (0.71, s) that gradually dropped and that of fluorotrimethylsilane (**6b**) (34.26, d, *J* = 273 Hz) that gradually increased in both

(22) For example, the 3-methyl group of a (*Z*)-crotylsilane, which points toward the inner part of the cyclic structure, would probably cause a stronger interaction with the O-BF₂ group in the tighter **A** than in the looser **B** structure.

cases. Recording of ^{13}C NMR spectra of a mixture of **1c**, **2b**, and **3b** showed **2b** (-2.2, 24.8, 112.5, 135.5), **6b** (-0.08, d, $J = 14.9$ Hz), free (15.4, 65.9) and boron-complexed (13.3, 69.9) diethyl ether, the borylated homoallylic product **5c** (14.4, 23.2, 25.8, 29.7, 29.9, 32.2, 33.8, 39.3, 78.3, 118.9, 133.0), and another set of signals¹⁴ (14.1, 22.9, 25.7, 29.5, 29.7, 32.1, 36.1, 41.2, 73.4, 117.3, 135.1) in a minor amount. For comparison we report the spectra of **8c** (1.1, 14.2, 23.0, 26.0, 29.6, 29.9, 32.2, 37.2, 42.3, 70.9, 117.6, 135.6) and of **4c** (14.2, 23.0, 26.0,

29.6, 29.9, 32.1, 37.2, 42.3, 70.9, 117.5, 135.5) obtained under the same conditions.

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