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Conformational Study of SnCl$_4$ Complexes of Aldehydes, α,β-Unsaturated Aldehydes, and Esters: Observation of Both s-Cis and s-Trans Isomers

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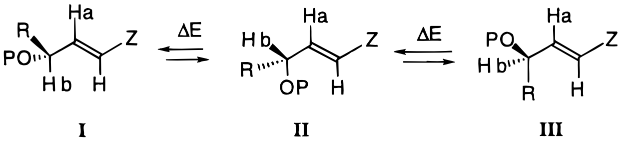
A variable-temperature NMR study shows that 2-methylpropanal (**1a**), ethyl 2-pentenoate (**2**), ethyl 4-methyl-2-pentenoate (**3a**), 2-pentenal (**4**), and 4-methyl-2-pentenal (**5a**) prefer the C-CH$_3$ eclipsed conformations, rather than the CH-eclipsed form. The preference is enhanced in the presence of SnCl$_4$. This is opposite to consideration based on steric interactions but is consistent with hyperconjugative interaction, in which the C−H bond is aligned with the $\pi^*_{C=C}$ orbital. Thus, the current result suggests that the C−H bond is a better donor than the C−C bond in hyperconjugation with electron-deficient π orbital. On the other hand, 2-ethylbutanal (**1b**), ethyl 4-ethyl-2-hexenoate (**3b**), and 4-ethyl-2-hexenal (**5b**) prefer the CH-eclipsed form due to steric effects. At −50 °C, the SnCl$_4$ complexes of **3a** and **3b** show two distinct sets of vinyl protons in a ratio of ~10:1, which are assigned to the s-trans- and s-cis isomers, respectively.

Introduction

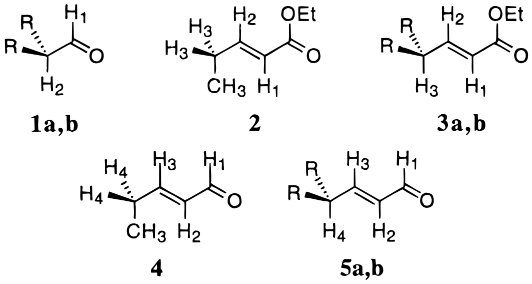
Recently, we have reported the results from a systematic study using both *ab initio* molecular orbital methods and variable-temperature (VT) NMR technique for the conformations of chiral alkenes.[1] Our study confirmed Hehre's early predictions about the influence of the substituent at vinyl position on the ground state conformations of chiral alkenes: "...it is to be expected that electron-withdrawing group (EWG) will favor conformations with the CO bond eclipsing $\pi_{C=C}$, whereas electron-releasing group (ERG) should enhance the ground-state preference for the CH eclipsing the double bond."[2]



I is favored when Z = alkyl; **II** is favored when Z = CN or CO$_2$R'

In our previous study, the VT NMR evidence also suggested the presence of conformation **III**.[1a] We were somewhat surprised because form **III** should be sterically inhibited due to $A^{1,3}$ strain.[3] In order to clarify the relative stability of **III** with respect to the steric bulk of the R group, we have studied compounds **1**−**5** (Chart 1) and their SnCl$_4$ complexes. There is a clear difference in conformational preference between the methyl (R = Me, **1a**, **2**, **3a**, **4**, **5a**) and the ethyl (R = Et, **1b**, **3b**, and **5b**) derivatives. The CC-eclipsed conformation (**III**) was found to be more stable than the CH-eclipsed form in the cases of the methyl derivatives. The opposite is true for the ethyl derivatives. In addition to these observations, we have also been able to observe both the s-trans and the s-cis isomers for the SnCl$_4$ complexes of esters **3a**,**b** by ^{1}H NMR at low temperature. This is of significant interest since in many cases the goal of obtaining high enantioselectivity in nucleophilic addition to α,β-unsaturated ester system depends on our understanding and control of the conformation.[4−11]

Chart 1



a: R = CH$_3$, **b**: R = CH$_2$CH$_3$

In a related issue, there has been a continuing debate on the relative donor ability of C−C vs. C−H bonds in organic molecules.[12−16] Cieplak suggested that the C−H bond is a better donor than the C−C bond on the basis

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(1) (a) Gung, B. W.; Wolf, M. A.; Zhu, Z. *J. Org. Chem.* **1993**, *58*, 3350−3354. (b) Gung, B. W.; Wolf, M. A. *J. Org. Chem.* **1993**, *58*, 7038−7044. (c) Gung, B. W.; Gerdeman, M. S.; Fouch, R.; Wolf, M. A. *J. Org. Chem.* **1994**, *59*, 4255−4261. (d) Gung, B. W.; Melnick, J. P.; Wolf, M. A.; Marshall, J. A.; Beaudoin, S. *J. Org. Chem.* **1994**, *59*, 5609−5613. (e) Gung, B. W.; Zhu, Z.; Fouch, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 1783−1788.

(2) Khan, S. D.; Pau, C. F.; Chamberlin, A. R.; Hehre, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 650.

(3) For a review, see: Hoffmann, R. W. *Chem. Rev.* **1989**, *89*, 1841.

(4) Loncharich, R. J.; Schwartz, T. R.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 14−23.

(5) Oppolzer, W.; Loher, H. J. *Helv. Chim. Acta* **1981**, *64*, 2808.

(6) (a) Oppolzer, W.; Chapius, C.; Bernardinelli, G. *Tetrahedron Lett.* **1984**, *25*, 5885. (b) Oppolzer, W.; Kelly, M. J.; Bernardinelli, G. *Tetrahedron Lett.* **1984**, *25*, 5889. (c) Oppolzer, W.; Rodriguez, I.; Blagg, J.; Bernardinelli, G. *Helv. Chim. Acta* **1989**, *72*, 123.

(7) Barnes, J. C.; Brimacombe, J. S.; Irvine, D. J. *Carbohydr. Res.* **1990**, *200*, 77.

(8) Poll, T.; Metter, J. O.; Helmchen, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 112.

(9) Wolff, S.; Venepalli, B. R.; George, C. F.; Agosta, W. C. *J. Am. Chem. Soc.* **1988**, *110*, 6785.

(10) Lewis, F. D.; Oxman, J. D.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 466.

(11) (a) Suzuki, I.; Kin, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **1993**, *115*, 10139−10144. (b) Shida, N.; Kubato, C.; Niwa, T.; Ebata, T.; Yamamoto, Y. *J. Org. Chem.* **1994**, *56*, 4068.

(12) (a) Cieplak, A. S.; Tait, B. D.; Johnson, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 8447. (b) Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540.

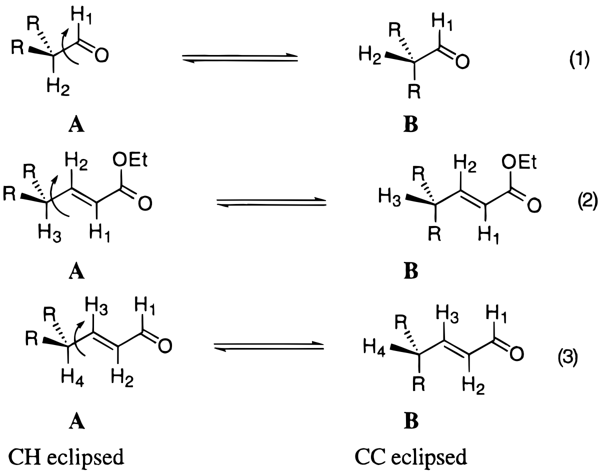
(13) (a) Roseboom, M. D.; Houk, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 1189. (b) Dorigo, A. E.; Pratt, D. W.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 6591. (c) Broeker, J. L.; Hoffmann, R. W.; Houk, K. N. *J. Am. Chem. Soc.* **1991**, *113*, 5006.

0022-3263/96/1961-0947$12.00/0

of the Baker–Nathan order.[12] However, Houk indicated that the C–C bond is a better donor on the basis of the fact that the ionization potentials in a series of piperidines decrease in a nonlinear fashion.[13a] Whether the origin of the Baker–Nathan effect is hyperconjugative has been disputed. Differential solvation was suggested as the reason for the observed rate order.[14] Thus, the order of hyperconjugation ability for alkyl groups was also questioned. The stereochemical results from some rigid cyclic ketones also cast doubt on the relative donor ability of CH vs. CC bonds.[15]

However, recent evidence seems to indicate that hyperconjugative electron donation by σ_{CH} bonds is larger than that by σ_{CC} bonds. Laube has reported a theoretical study concerning hyperconjugation in substituted acetaldehydes.[16a] On the basis of X-ray structure data and *ab initio* calculations at the 4-31G* level, the potential energy curves for rotation about the C_{sp2}–C_{sp3} bond of substituted acetaldehydes are obtained. The least-squares adjustment of a truncated Fourier series allows a separation of the potential energy into a 1-fold (dipolar and steric interactions), a 2-fold (hyperconjugative interactions), and a 3-fold term (bond electron repulsions). A comparison of the V2 coefficients shows the following order of hyperconjugation: CH > CC > CCl > CF. On the basis of the X-ray structure of the $SbCl_5$-complexed 5-phenyladamantanone, Laube also concludes that a CH bond is a better donor than a C_{sp3}–C_{sp2} bond.[16b]

We figured that the conformational preference of compounds **1**–**5** can be used to judge the donor ability of C–H/C–C bonds. Rotation around the C_{sp2}–C_{sp3} bond can lead to either the CH-eclipsed form (**A**) or the C–C-eclipsed form (**B**). The better donor bond would prefer to align with the π* orbital, rather than the C=C bond, on the basis of the hyperconjugative model.[13b,16a]



Using the VT NMR technique, we were able to determine which bond is eclipsed with the C=C linkage by recording the coupling constants of the $C_{sp2}H$–$C_{sp3}H$ rotamer.[1] The CH-eclipsed form (conformer **A**) should give a greater coupling constant ($^3J_{12}$, $^3J_{23}$, $^3J_{34}$ for eqs 1, 2, 3, respectively) than the C–C-eclipsed conformation (**B**). In a rapid equilibrium mixture, a weighted average of the coupling constants will change with the populations of the conformers. As the temperature is lowered, the more stable conformation will become more populated. Therefore, the more stable conformer is found through examining the relationship of coupling constant with temperature.[17]

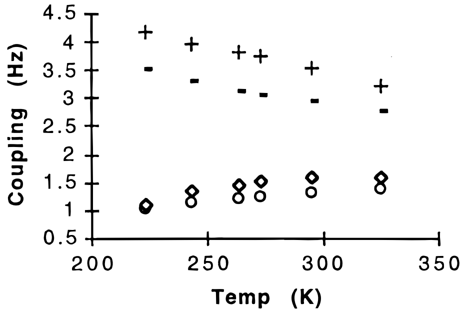


Figure 1. Coupling constants ($^3J_{12}$) as a function of temperature for aldehyde **1a** (○), $SnCl_4$·**1a** (◇), **1b** (–), and $SnCl_4$·**1b** (+).

Experimental Section

Esters **2** and **3a**,**b** (Chart 1) are prepared from propanal, 2-methylpropanal (**1a**), and 2-ethylbutanal (**1b**), respectively, by treatment with Wittig reagent (Ph_3P=$CHCO_2Et$). The α,β-unsaturated aldehydes **4** and **5a**,**b** are obtained through reduction of **2** and **3a**,**b** with DIBAL-H, respectively, followed by oxidation with the Swern procedure.[18] The NMR experiments involve the measurements of the three-bond ($^3J_{12}$, $^3J_{23}$, $^3J_{34}$) proton coupling constants of compounds **1**–**5** at various temperatures and subsequent analysis using the *J*-averaging method.[17] The details of the VT NMR experiments follow the early reports.[1] Briefly, the ^{1}H NMR spectra were recorded on a Bruker 300 MHz instrument with a variable-temperature probe. The samples were degassed before each run, and the concentration was about 0.05 M. The variable-temperature data were reproducible to ±0.02 Hz in duplicate runs. Deuterated chloroform was used in these experiments. The $SnCl_4$ complexes of compounds **1**–**5** were freshly prepared in a ratio of 1:1 before each experiment under nitrogen atmosphere.

Results and Discussion

A. Steric and Hyperconjugative Effects on The Conformations of Compounds 1–5 and Their $SnCl_4$ Complexes. The variable-temperature NMR data are summarized in Figures 1–5 and Figure 8. The three-bond coupling between the aldehydic proton and the α proton ($^3J_{12}$) of aldehydes **1a**,**b** (Figure 1) gives a measure for the equilibrium shown in eq 1. Similarly, the coupling constants between the vinylic proton and the allylic proton ($^3J_{23}$) of esters **2** and **3a**,**b** (Figures 2 and 3) are measures for the equilibrium shown in eq 2. The $^3J_{34}$ of aldehydes **4** and **5a**,**b** (Figures 4 and 5) corresponds to the rotation shown in eq 3.

According to the data in Figure 1, when R = Me (**1a**) the coupling constants are small and decrease as temperature is lowered. This indicates a shift of population toward conformation **B** at lower temperatures. Therefore, the methyl-eclipsed form (**B**) is more stable than the CH-eclipsed form (**A**). This is consistent with the

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(14) (a) Schubert, W. M.; Sweeney, W. A. *J. Org. Chem.* **1956,** *21*, 119. (b) Hehre, W. J.; McIver, Pople, J.; Schleyer, *J. Am. Chem. Soc.* **1974,** *96*, 7162.

(15) Li, H.; Mehta, G.; Padma, S.; le Noble, W. J. *J. Org. Chem.* **1991**, *56*, 2006.

(16) (a) Laube, T.; Ha, T.-K. *J. Am. Chem. Soc.* **1988**, *110*, 5511. (b) Laube, T.; Stilz, H. U. *J. Am. Chem. Soc.* **1987**, *109*, 5876.

(17) For examples of the application of the J-averaging method, see: (a) Bothner-By, A. A.; Castellano, S.; Ebersole, S. J.; Gunther, H. *J. Am. Chem. Soc.* **1966**, *88*, 2466. (b) Copley, S. D.; Knowles, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 5008.

(18) Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165.

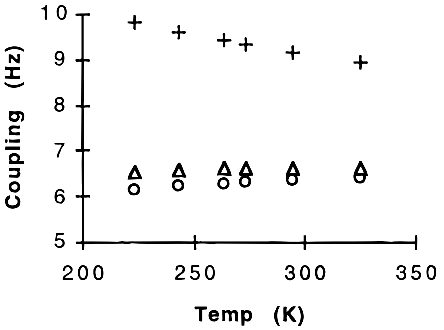


Figure 2. Coupling constants ($^3J_{23}$) as a function of temperature for esters **2** (○), **3a** (△), and **3b** (+).

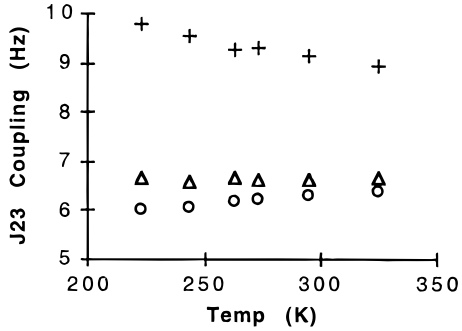


Figure 3. Coupling constants ($^3J_{23}$) as a function of temperature for the $SnCl_4$ complexes of esters **2** (○), **3a** (△), and **3b** (+).

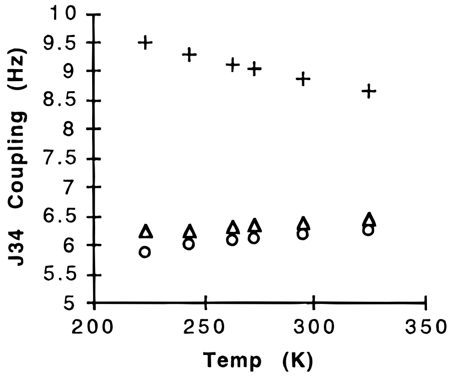


Figure 4. Coupling constants ($^3J_{34}$) as a function of temperature for aldehyde **4** (○), **5a** (△), and **5b** (+).

results from previous studies on the conformations of propanal and 2-butanone.[19]

When R = Et (**1b**), the coupling constants (Figure 1) are much larger than that of **1a** and increase as temperature is lowered, which means that the CH-eclipsed form (**A**) is favored. We interpret the difference between the methyl and the ethyl derivatives as steric effects. As shown below (**C**), a 1,3-close contact between the terminal methyl group and the aldehydic proton and between the other methyl group and the carbonyl oxygen is present if the C═O is eclipsed with the ethyl group in **1b**. This analysis is confirmed by the observation that $^3J_{12}$ of **1b** increases when **1b** is complexed with $SnCl_4$ (Figure 1). The reason for this increase in magnitude of coupling is the increased steric bulk around the carbonyl oxygen atom, which further raises the repulsive interaction shown below (**C**). Thus, the preferred conformation for **1b** is the CH-eclipsed form (**B**).

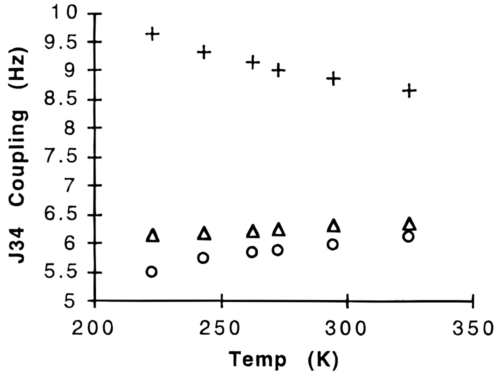
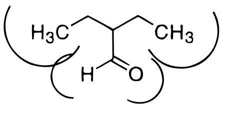
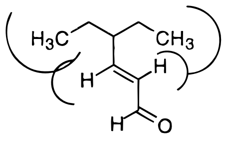


Figure 5. Coupling constants ($^3J_{34}$) as a function of temperature for the $SnCl_4$ complexes of aldehyde **4** (○), **5a** (△), and **5b** (+).



C



D

This divergent behavior between the methyl and the ethyl derivatives is also observed for the α,β-unsaturated esters **3a**,**b** (Figures 2 and 3) and aldehydes **5a**,**b** (Figures 4 and 5). The differences in the magnitude of coupling between **3a** and **3b** and between **5a** and **5b** are even greater, but complexation of $SnCl_4$ did not change the coupling constants for **3b** and **5b**. These facts are consistent with the 1,3-interactions shown above for **5b** (**D**). Clearly, a CH-eclipsed form (**A**) is favored for **5b** if the pentane carbon chain in **5b** is to remain in the preferred all-anti conformation.

On the basis of the steric effects described above, it is expected that the ethyl derivatives (**1b**, **3b**, and **5b**) prefer the CH-eclipsed form (**A**). However, it is uncertain why the methyl derivatives (**1a**, **2**, **3a**, **4**, **5a**) favor the CC eclipsed form (**B**). Wiberg has indicated that the preference for an alkyl group to be eclipsed with a C═O bond in an aldehyde or a ketone is probably due to dipole induced-dipole interaction.[18] However the data are not inconsistent with hyperconjugative effects,[13b,16a] such as the overlap between the allylic σ_{CH} and $\pi^*_{C=C}$ orbitals. This overlap is possible only when the CH bond is in the skew position, Figure 6. The fact that the C−C bond is eclipsed with the C═C linkage is consistent with the C−H bond being a better donor.

It is known that the CH-eclipsed forms of 1-butene and 3-methyl-1-butene are more stable than their methyl-eclipsed form by ∼0.25[18] and ∼0.75[13c] kcal/mol, respectively. Although these results are in contrast to our current observations for the α,β-unsaturated aldehydes and esters, an argument can be made to support the hyperconjugative concept. Hyperconjugation is most pronounced when there is a positive charge, such as in the case of a carbocation, next to CH bonds. 1-Butene and 3-methyl-1-butene have an electron neutral double bond, but the α,β-unsaturated aldehydes **5** and esters **3** are electron-deficient alkenes. Thus, different degrees of demands for hyperconjugation exist in these alkenes. It is reasonable to assume that the α,β-unsaturated aldehydes **5** and esters **3** are stabilized by hyperconjugative interactions more than that for 1-butene and 3-methyl-1-butene.

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[19] Wiberg, K. B.; Martin, E. *J. Am. Chem. Soc.* **1985**, *107*, 5035.

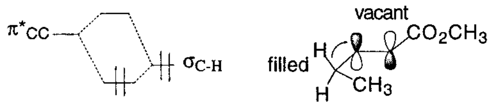
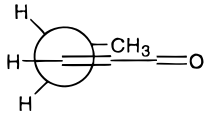


Figure 6. Stabilizing interaction between the σ_{CH} bond and the $\pi^*_{C=C}$ orbital in methyl 2-pentenoate.

In cases where 1 equiv of $SnCl_4$ is added to the $CDCl_3$ solution of the carbonyl compounds, a slight enhancement in the trend is observed. For example, aldehyde **4** exhibits three-bond coupling $^3J_{34}$ from a range of 6.25 Hz at 325 K to 5.88 Hz at 223 K ($\Delta J/\Delta T = 0.0036$). Its $SnCl_4$ complex has coupling constants of 6.11 Hz at 325 K and 5.48 Hz at 223 K ($\Delta J/\Delta T = 0.0062$). Thus, the $SnCl_4$ complex has both smaller coupling constants and greater temperature coefficient, which indicates a greater stability of the methyl-eclipsed conformer (**B**). The hyperconjugative effect is more pronounced in the Lewis acid complex since $SnCl_4$-complexation reduces the electron density of the double bond and lowers the energy of the $\pi^*_{C=C}$ orbital.

It should be noted that the other $SnCl_4$ complexes examined in this study (other than **4**) show negligible changes in their coupling constants. This is probably due to the fact that the methyl-eclipsed form (see below) of aldehyde **4** enjoys two skew CH bonds while the conformation **B** of **3a** and **5a** have only one CH bond in the skew position to participate in hyperconjugation. The stabilization of a conformation resulted from a CH bond participating in hyperconjugation with the $\pi^*_{C=C}$ orbital is only slightly greater than that from a CC bond. Currently, we prefer the hyperconjugative model since the dipole induced−dipole theory does not give a better explanation of the data.



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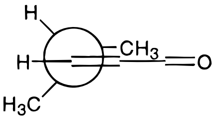

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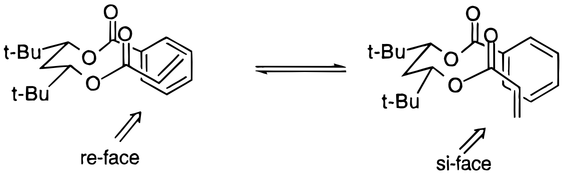
B. Observation of the s-Cis and the s-Trans Isomers. The interconversion of the s-trans and s-cis forms of α,β-unsaturated esters has been a concern of synthetic organic chemists for a long time because opposite π-face selectivity results from s-trans and s-cis forms.[5−11] Illustrated below is an example recently reported by Yamamoto.[11]



Although X-ray structures of acrylates have been reported,[5−11] the dynamics of s-trans/s-cis isomerization in solution have rarely been studied. One reason for the lack of study might be the lack of proper tools.

During our work on $SnCl_4$-complexed α,β-unsaturated esters, it was discovered that the barrier to rotation in complex **3a** was considerably higher than that of the free ester. At −40 °C, the s-trans and the s-cis isomers give distinct ^1H NMR spectra (Figure 7). A ratio of approximately 93:7 can be determined by integration of the ^1H NMR. On the basis of previous experimental[5−11] and theoretical[4] studies, the major isomer is assigned the s-trans conformation. The coalescence temperature for s-trans/s-cis isomerization is ∼−25 °C (Figure 7). By using the approximate equation (eq 4)[20,21] and extrapolat-

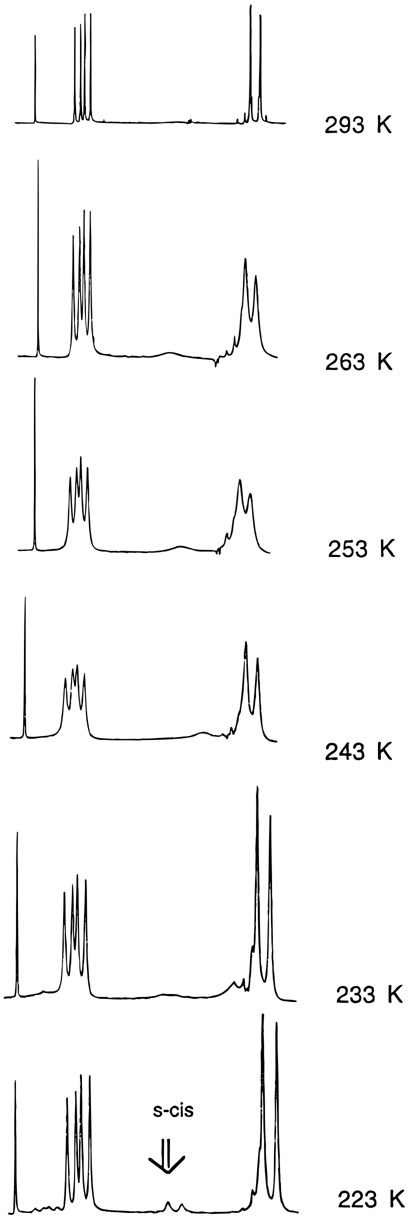
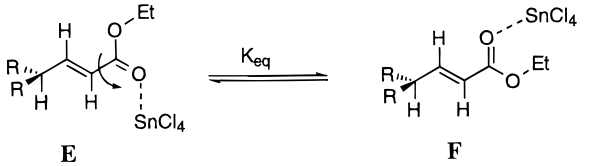


Figure 7. Vinyl region of the proton NMR spectra of ethyl 4-methyl-2-pentenoate complexed with 1 equiv of $SnCl_4$ at various temperatures.



E
s-trans

F
s-cis

R = CH_3, CH_2CH_3

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[20] (a) Binsch, G. In *Topics in Stereochemistry*; Eliel, E. L., Allinger, N. L., Eds,; Wiley: New York, **1968**; Vol. 3, p 97. (b) Sutherland, I. O. In *Annual Reports on NMR Spectroscopy*; Mooney, E. F., Ed.; Academic Press: London, 1971, *4*, 71−235.

[21] (a) Jackman, L. M.; Cotton, F. A. *Dynamic Nuclear Magnetic Resonance Spectroscopyp*; Academic Press: New York, 1975. (b) Binsch, G. *J. Am. Chem. Soc.* **1969**, *91*, 1304. (c) Iwamura, M. Katoh, M.; Iwamura, H. *Org. Magn. Reson.* **1980**, *14*, 392−397.

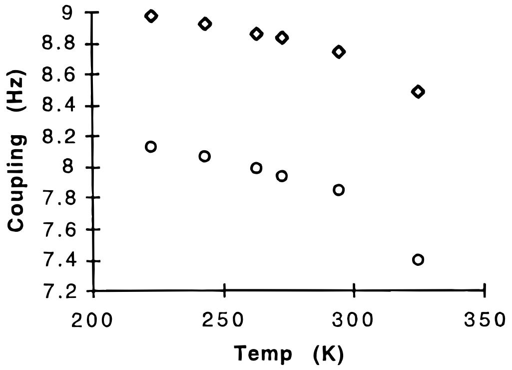


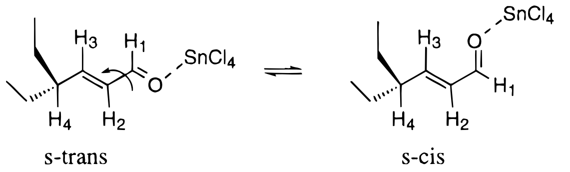
Figure 8. Coupling constants ($^3J_{12}$) as a function of temperature for aldehyde **5a** (○) and $SnCl_4$·**5a** (◇).

ing the v_{ab} from several Δv's at lower temperatures to the coalescence point, the barrier to rotation for the complex is ~12.5 kcal/mol using the Eyring equation (eq 5).[20,21]

$$k_c = \frac{\pi \nu_{ab}}{\sqrt{2}} = 2.22\nu_{ab} \quad (4)$$

$$\Delta G^{\ddagger} = 2.303RT\left(10.319 + \log\frac{T}{k}\right) \quad (5)$$

Unlike the $SnCl_4$-complexed acrylates, rapid equilibrium still occurs between the s-trans and s-cis isomers of $SnCl_4$-complexed α,β-unsaturated aldehydes at or above −50 °C. No coalescence was observed for these complexes. However, it is also of significance to uncover the relative stability of these isomers. For example, Corey has demonstrated the importance of understanding the detailed structure of Lewis acid-complexed acrolein in relation to enantioselectivity and has shown that BF_3-complexed 2-methylacrolein has the s-trans conformation, yet the enantioselective Diels−Alder cycloadditions occur through the s-cis form.[22] Denmark has shown that the s-trans conformation is the predominant form for the complex of 2-heptenal with $SnCl_4$ by using nuclear Overhauser difference spectroscopy.[23]



No coalescence was observed at -50 °C

The calculated energy difference between s-trans and s-cis acrolein is 1.8 kcal/mol at the 6-31G*//3-21G level of theory.[4] Lithium-complexed acrolein gives a difference of 3.2 kcal/mol.[4] According to these calculated numbers, Lewis acid-complexed α,β-unsaturated aldehydes assume almost exclusively the s-trans form. However, Marshall has shown that the addition of chiral allylstannanes to a chiral α,β-unsaturated aldehyde occurs most likely through the s-cis form.[24] The current results are consistent with both Corey and Denmark's observations; i.e., the s-trans isomer is preferred in solution. Complexation with $SnCl_4$ enhances this preference. All three α,β-unsaturated aldehydes (**4**, **5a**,**b**) exhibit the same trend as that shown in Figure 8 for **5a**. The significant increase of the magnitude in coupling constant from free aldehyde to complex is consistent with a greater population of s-trans isomer for the complex. However, since no coalescence was observed, the rotation around the C−C bond must be fast. This means the s-cis isomer is available for reaction. Thus, according to Curtin−Hammett principle,[25] the experimental observations of both Corey and Marshall can be interpreted as this: the s-cis isomer must be the more reactive conformation. In fact, this has been suggested in the literature.[4]

Conclusion

By using the variable-temperature NMR technique, it is found that aldehyde **1a**, α,β-unsaturated esters **2** and **3a**, and α,β-unsaturated aldehydes **4** and **5a** and their $SnCl_4$ complexes prefer the methyl-eclipsed conformation (**B**), rather than the C−H-eclipsed form (**A**). This phenomenon is discussed in terms of hyperconjugative interactions between the better donor C−H bond and the π* orbital. The C−C bond is not as good a donor as the C−H bond. Therefore, the methyl-eclipsed form is more stable for these electron-deficient alkenes. The ethyl derivatives (**1b**, **3b**, and **5b**) favor the CH-eclipsed form as expected on the basis of steric effects. The predominant conformation for $SnCl_4$-complexed α,β-unsaturated esters is the s-trans form. The rotational barrier around the C_{sp2}−C_{sp2} bond in a $SnCl_4$ complexed α,β-unsaturated ester is about 12.5 kcal/mol. The rotation around this bond is slower than the NMR time scale at or below −40 °C. On the other hand, the rotation around the same bond is still fast for the $SnCl_4$-complexed α,β-unsaturated aldehydes at this temperature.

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Supporting Information Available: Variable temperature ^1H NMR data for compounds **1**−**5** (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[22] (a) Corey, E. J.; Loh, T.-P. *J. Am. Chem. Soc.* **1991**, *113*, 8966. (b) Corey, E. J.; Loh, T.-P.; Roper, T. D.; Azimioara, M. D.; Noe, M. C. *J. Am. Chem. Soc.* **1992**, *114*, 8290. (c) Corey, E. J.; Loh, T.-P.; Sarshar, S.; Azimioara, M. *Tetrahedron Lett.* **1992,** *33*, 6945.

[23] Denmark, S. E.; Almstead, N. G. *J. Am. Chem. Soc.* **1993**, *115*, 3133−3139.

[24] Marshall, J. A.; Beaudoin, S. *J. Org. Chem.* **1994**, *59*, 7833. See also: Wong, S. S.; Paddon-Row, M. N.; Li Y.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 8679.

[25] Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83.