Epimerization Study on the Mixture of Lactones 15 and 17. To a solution of 66 mg (0.18 mmol) of the mixture of epimeric lactones **15** and **17** (ratio 43:57 by ^{1}H NMR) in 30 mL of benzene was added 10 μL of DBU. The reaction mixture was stirred at 25 °C for 72 h, at which time it was poured into 80 mL of ethyl acetate, and the organic layer was washed with 0.5 N HCl. The organic layer was dried ($MgSO_4$) and concentrated. Integration of the methine resonances at δ 3.79 and 3.86 in the ^{1}H NMR showed that the ratio of **15** to **17** had increased to 59:41. This new mixture was redissolved in 30 mL of benzene, and 10 μL of DBU was added. The reaction mixture was heated at 52 °C for 56 h, cooled, and poured into 150 mL of ethyl acetate. After having been washed with 2.5% aqueous HCl, the organic layer was dried ($MgSO_4$) and concentrated. Integration of the ^{1}H NMR resonances at δ 3.79 and δ 3.86 for **15** and **17**, respectively, showed that the ratio had further increased to 80:20 in favor of **15**.

Acknowledgment. We are grateful to the National Institutes of Health and to Research Corp. for their generous support of this research. High-field NMR spectra were obtained through the National Science Foundation Regional NMR Center at the University of South Carolina (Grant CHE 78-18723). We acknowledge the experimental contributions of William R. Sutton in the early stages of this investigation.

Registry No. 4a, 87763-61-9; **4b**, 87763-62-0; **4c**, 87763-63-1; **4d**, 82731-58-6; (±)-**5a**, 87763-64-2; (±)-**5b**, 87763-65-3; (±)-**5c**, 87763-66-4; (±)-**5d**, 71215-27-5; **6a**, 87763-67-5; **6b**, 87763-68-6; **6c**, 87763-69-7; **6d**, 85970-67-8; (±)-**7a**, 87763-70-0; (±)-**7b**, 87763-71-1; (±)-**7c**, 87763-72-2; (±)-**7d**, 71215-25-3; (±)-**8a**, 87763-73-3; (±)-**8b**, 87763-74-4; (±)-**9a**, 87763-75-5; (±)-**9b**, 87763-76-6; (±)-**10**, 87763-84-6; (±)-**11**, 87763-77-7; (±)-**12**, 83057-87-8; (±)-**13**, 87763-78-8; (±)-**14**, 87828-38-4; (±)-**15**, 87763-79-9; (±)-**16** (isomer 1), 87763-80-2; (±)-**16** (isomer 2), 87763-85-7; (±)-**17**, 87828-39-5; $MEMOCH_2CO_2Et$, 87763-81-3; (benzyloxy)acetyl chloride, 19810-31-2; (*E*)-2-buten-1-ol, 504-61-0; 2-butynyl 2-methoxyacetate, 87763-82-4; 2-butynyl 2-[(2-methoxyethoxy)methoxy]acetate, 87763-83-5; 2-methoxyacetyl chloride, 38870-89-2; 2-butyn-1-ol, 764-01-2.

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^{19}F NMR Study on the Conformation Changes of 1,1,2,2-Tetrafluoro-1,2-disilacyclohexanes

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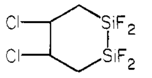
Four 1,1,2,2-tetrafluoro-1,2-disilacyclohexane derivatives are synthesized. The conformation changes associated with ring inversion of these compounds are studied by full line-shape analyses of their ^{19}F DNMR spectra. The activation parameters, ΔG^*, ΔH^*, and ΔS^*, are obtained with reasonable accuracy. The results show that the activation energy barrier of the ring inversion process is closely affected by the nature of the substituents at the 4 and 5 positions in cis orientation. A plausible mechanism for the ring inversion process, which involves a semiplanar transition state and a boat form intermediate, is proposed.

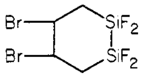
The use of DNMR full line-shape analysis for investigation of conformational equilibria and rates of ring inversion in cyclic compounds is well-known.[1] A great number of cyclohexane derivatives and other ring systems have been studied by this method, the results have provided valuable insight to the mechanisms of conformational changes in ring systems which are difficult to obtain by other methods.[1] Information about heterocyclic compounds is comparatively less complete; for example, there have been only a few studies on silacyclic compounds in the literature.[2,3] One of the reasons is that, unlike the cyclohexane system in which the stable form of the ring structure is well-known, the information of the basic static structures of heterocyclic compounds is often lacking. Besides, within the temperature range that the DNMR technique normally accesses, strained ring compounds often can not exibit their low temperature limiting spectra for analysis.

It is usually possible to work with much larger chemical shifts by replacing one or more hydrogens on a cyclic compound by fluorine atoms and study the ^{19}F NMR spectra. This "fluorine labeling" technique has already been used for determination of the rate of ring inversion of a number of fluorocyclic compounds.[4]

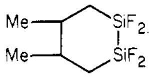
In the present study, ^{19}F NMR spectroscopy was used for studying the conformation change of four 1,1,2,2-tetrafluoro-1,2-disilacyclohexane derivatives I to IV, among



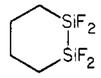
cis-I



cis-II



cis-III



IV

which the structure of I has been determined by a single crystal X-ray diffraction study,[5] and compound II has not been reported previously.

Experimental Section

Preparation of Compounds I, III, and IV. Compounds I, III, and IV were prepared and purified following the procedures reported previously.[6-8] Purification of III was improved by GC separation.

Preparation of Compound II. Compound II was obtained from the cocondensation reaction of difluorosilylene with vinyl bromide. The reaction and purification conditions were very similar to those used in the reaction of difluorosilylene with vinyl

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Table I. ^{19}F NMR Parameters of I, II, and III[a]

compd	chemical shift, ppm				coupling constant, Hz					
	ν_A	ν_B	ν_C	ν_D	AB	AC	AD	BC	BD	CD
I	136.1	137.4	140.8	141.0	13.70	10.34	2.07	4.30	7.93	10.13
II	136.0	137.2	139.5	139.9	13.31	11.09	2.03	4.28	8.48	10.40
III	134.5	137.2	139.5	142.7	14	10.6	2.4	4.0	8.1	11

[a] Coupling constants of III were estimated by averaging the corresponding coupling constants of I, II, and the values in ref 8.

chloride. Compound II was obtained by vacuum sublimation. Its mass spectrum showed M − Br$^+$ (*m/e* 265) and fragment ions $Si_2F_4Br^+$ (211), $C_4H_6SiF_2Br^+$ (199), $C_4H_5Si_2F_4^+$ (185), $C_2H_3SiFBr^+$ (153), $C_4H_6SiF_3^+$ (139), $C_4H_5SiF_2^+$ (119), and $C_4H_6SiF^+$ (101). The molecular ion was not observed at 12 eV electron impact. The molecular formula was further confirmed by elemental analysis. Anal. Calcd: C, 13.95; H, 1.74. Found: C, 13.91; H, 1.84. The NMR data of II are summarized as follows: ^{1}H δ 2.1 (br) and δ 4.7 (br), with intensity ratio 2:1. ^{13}C δ 29.3 (m) and δ 54.5 (s). ^{19}F 136.0, 137.2, 139.5, and 139.9, complex ABCD spectrum at −85 °C.

Spectra. Mass spectra were recorded on a JEOL JMS-100 mass spectrometer operating at 12 eV. All NMR spectra were recorded on a JEOL JNM FX-100 spectrometer operating at 99.5, 25.0, and 93.7 MHz for proton, carbon, and fluorine, respectively. Chemical shifts of ^{1}H and ^{13}C spectra were in δ values for ^{19}F spectrum they were measured upfield from the internal standard CCl_3F. For I, II, and III, *n*-pentane/$CDCl_3$ in a 1:1 ratio was used as the solvent; for compound IV, a mixture of $CDCl_3$/CF_2CFCl/CH_2CHF in the ratio of 3:4:2 was used. Typical operation conditions were: pulse width 16 μs, pulse interval 8 s, scans 9, and spectrum width 1000 Hz with 8192 data points.

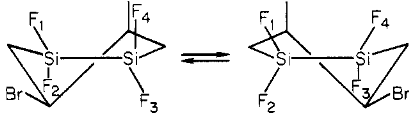
Temperature Measurement. Temperatures were calibrated by inserting a copper-constant thermocouple into the sample probe and measured against the reference temperature of ice/water. The temperature range being calibrated was from −120 to 110 °C. The readings were taken simultaneously with the recording of the spectra and are accurate to ±0.2 °C at the sample.

Temperature effect on the relative chemical shifts of the limiting spectra was found to be not very significant; the spectra data were not corrected.

Computer Calculations. Computer calculations were performed on a CDC cybe 172 computer. The DAVINS[9] program was used for the full analysis of low temperature limiting spectra; the DNMR5[9] program was used for the analysis of dynamic spectra.

Results and Discussions

Compounds I and II reached limiting spectra at −90 and −80 °C, respectively. At −102 °C, the peaks of the four fluorines in compound III were well separated and seemed not to change any further; however, fine structures of the peaks were not resolved. They all exibited complex ABCD spectra as was expected for half-chair conformations. The ABCD spectra are analyzed and the spectral parameters are listed in Table I. The six F–F coupling constants can be classified into three categories: (i) for J_{AD} and J_{BC}, 3 ± 1 Hz, (ii) for J_{AC} and J_{BD}, 9 ± 2 Hz, and (iii) for J_{AB} and J_{CD}, 12 ± 2 Hz. These values agree reasonably well with the literature values for $^3J_{cis}$, $^3J_{trans}$, and $^2J_{gem}$ of tetrafluorodisilacyclic compounds, respectively.[10] We use the spectrum of II to illustrate the spectral features.



(e,a) (a,e)

Table II. Kinetic Parameters of Compounds I, II, III, and IV

compd	T_c, °C[a]	Δ$H^‡$, kcal mol^{-1}	Δ$G^‡$, kcal mol^{-1}	Δ$S^‡$, eu
I	−9.8	7.17 (5)	12.14 (2)	−18.9 (1.6)
II	−1.5	7.77 (5)	12.72 (3)	−18.2 (1.5)
III	−89.1	5.22 (40)	8.40 (9)	−17.8 (1.8)
IV	−114		6.3 (1)	

[a] Coalescence temperatures for I, II, and III; the lowest experimental temperature for IV.

The two conformers of the cis configuration are indistinquishable. The chemical environments of the four fluorines are different. As the ring inverts, the fluorines exchange their chemical environments in pairs, i.e., $F_1 \rightleftarrows F_4$ and $F_2 \rightleftarrows F_3$. The proton-noise decoupled ^{19}F limiting spectrum shows four complex peaks of equal intensity at 136.0 (A), 137.2 (B), 139.5 (C), and 139.9 ppm (D), respectively. As temperature rises, the peaks become broadened and overlapped into two peaks representing the average of $F_1 \rightleftarrows F_4$ and $F_2 \rightleftarrows F_3$, respectively, but one cannot tell which peaks represent which pair of exchanging fluorines.

To confirm the assignment, spectra of different exchanging rates with $F_A \rightleftarrows F_D$ and $F_B \rightleftarrows F_C$ or $F_A \rightleftarrows F_C$ and $F_B \rightleftarrows F_D$ were calculated and compared with the experimental spectra; it was certain that the former exchange pair was the true one.

The Arrhenius plot of the calculated rate constant vs. reciprocal temperature gives at coalescence (−9.8 °C) the activation parameters Δ$G^‡$, Δ$H^‡$, and Δ$S^‡$ as 12.72 ± 0.03 kcal mol^{-1}, 7.77 ± 0.005 kcal mol^{-1}, and 18.2 ± 1.5 eu, respectively.

The ^{19}F NMR spectral parameters of compound I–III are listed in Table I. The kinetic parameters are listed in Table II.

The averaged spectrum with protons decoupled for compound IV at fast exchange is an A_4 singlet, the slow exchange spectrum should be an AA′XX′ spectrum. However, at −114 °C, the lowest temperature reached experimentally, the spectrum showed a broadened peak at 140 ppm. Obviously, the rate of exchange at −114 °C is still too rapid for observation of limiting spectrum. Full line-shape analysis is therefore not possible. By the use of the half-height width of the spectra and the chemical shift difference (4 ppm) proposed by Thompson et al.,[10] the exchange rates at various temperatures in a range from −66 to −114 °C were estimated. The procedure of estimation may introduce a considerable amount of error; however, the effect on the value of Δ$G^‡$ is relatively small.[11] The average value of Δ$G^‡$ over the temperature range is calculated to be 6.8 ± 0.5 kcal mol^{-1}. It is worth noting that the barrier for ring inversion in 1,1-dimethylsilacyclohexane was measured[2] to be 5.5 kcal/mol, and the upper limits of Δ$G^‡$ for 1,1,4,4-tetramethyl-1,4-disilacy-

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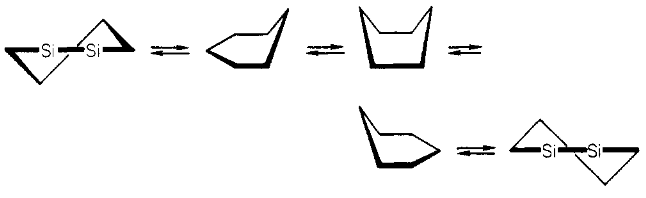
Scheme I



clohexane and 3,3-dimethyl-3-sila-1-heterocyclohexanes were estimated not to exceed 6.0 and 6.7 kcal/mol, respectively.[3] From the study of ring torsions it had been concluded that as the size of the heteroatom increased the region around the heteroatom tended to flatten, and this effect was compensated by a puckering of the opposite side of the ring.[3]

Compound I has been shown to have a half-chair structure by the single-crystal X-ray diffraction study.[5] The structure deviates considerably from the chair form of cyclohexane but resembles the stable conformation of cyclohexene.

All ring bond angles deviate from the standard tetrahedral values with the carbon bond angles (maximum 118.9°) showing greater deviation than the silicon ones, indicating the disilane part of the ring is considerably flattened. Like the case of cyclohexene, the inclusion of different bond lengths in the ring is the main source of the strain that leads to the half-chair conformation.

Single-crystal X-ray diffraction data for compounds II, III, and IV are not available. However, since the coupling constants calculated for these compounds are very similar to those of I, it is assumed that all four compounds have the same half-chair conformation.

The activation free energy, $\Delta G^{\ddagger}$, is 10.3 kcal mol^{-1} for cyclohexane and 5.3 kcal mol^{-1} for cyclohexene. The involvement of a short and planar double bond in the case of cyclohexene brings about steric strain which would lower the energy barrier of ring inversion.[15] For compound IV, the long Si–Si linkage would also cause considerable ring strain, so the activation free energy ($\Delta G^{\ddagger}$ = 6.3 kcal mol^{-1}) is also considerably lowered from that of the unstrained cyclohexane. The effect of fluorine substitution on the energy barrier of ring inversion is small.[12] In the case of IV, it is believed that the effect is even smaller than that in the carbon analogues because the dipolar interactions between the fluorines are expected to be smaller as the fluorines are separated farther in the $-SiF_2-SiF_2-$ linkage.

If the activation free energies of I, II, III and IV are compared, it seems that the substitutions at the 4 and 5 positions have significant influence on $\Delta G^{\ddagger}$'s (Table II). At coalescence temperatures, $\Delta G^{\ddagger}$ for I, II, III, and IV are 12.14, 12.72, 8.40, and ≤6.3 kcal mol^{-1}, respectively. Both steric and dipolar interactions of the substituents must have played some roles in these cases.

A structural model study shows that, if a nearly planar conformation is assumed for the transition state of the ring inversion process, the neighboring substituents at cis orientation become eclipsed. Taking the bond length of C_4–C_5 from the structure of I (1.56 Å), one can see that a considerable amount of steric interaction must exist in compounds I, II, and III because the van der Waal radii of Cl, Br, and CH_3 are 1.81, 1.95, and 2.0 Å, respectively.[13] These steric interactions would increase the inversion energy barrier; in the case of III, the increase is about 2 kcal mol^{-1}. For compounds I and II, additional dipolar interactions must be considered. The effect is an additional increase in the energy barrier of 4∼4.5 kcal mol^{-1}, which makes the $\Delta G^{\ddagger}$ of I and II 12.14 and 12.72 kcal mol^{-1}, respectively.

It is interesting to note, for cyclohexane systems, that the disubstitution on neighboring carbons has a rather small effect on the $\Delta G^{\ddagger}$ values.[14] This is because in the cases of cyclohexanes no eclipsed transition state in the ring inversion process of a standard chair form conformation is involved.

On the basis of the arguments given above, one can propose a plausible mechanism for the ring inversion process of 1,2-disilacyclohexanes: the half-chair conformer of 1,2-disilacyclohexane inverts via a semiplanar transition state with one carbon out of the plane with a boat form as the intermediate. The semiplanar form of cyclohexane has C_s symmetry and has often been considered as a possible transition state because it is only slightly higher in energy than the half-chair form, as shown by a full force-field calculation.[16] The process is illustrated in Scheme I.

The entropy of activation, $\Delta S^{\ddagger}$, is a measure of the molecular symmetries, vibrational modes, and rotational modes of the ground state and transition state. For the three 1,2-disilacyclohexanes studied, the $\Delta S^{\ddagger}$ values are quite similar i.e., −18 eu. The values of entropy of activation for cyclohexane systems are normally very small, but fluorine substitution may cause large negative $\Delta S^{\ddagger}$ values. For example, the $\Delta S^{\ddagger}$ for 1,1,2,2-tetrafluorocyclohexane is −13.6 ± 2 eu.[4] It is found that tetrafluorodisilacyclohexanes studied in this work showed considerable interaction with halogen-containing solvents; for example, the ^{19}F NMR spectra of these compound showed quite different chemical shifts and therefore different spectral patterns in chloroform as compared to those in *n*-pentane. Besides, crystalline compounds I and II become viscous oils and could not be recovered as crystals in chloroform solution even after the solvent had been removed by prolonged pumping. The value of $\Delta S^{\ddagger}$ as large as −18 eu seems very unusual, and hence both the solvent effect and the semiplanar transition state must have contributed to it. In view of the temperature effect on ^{19}F chemical shift, which was not corrected in this work, the possibility that some systematic error was involved could not be ruled out.

Acknowledgment. We thank the Chinese National Science Council for financial support of this work and Dr. T. H Hseu for helpful discussions.

Registry No. *cis*-I, 70787-84-7; *cis*-II, 87413-12-5; *cis*-III, 78844-46-9; IV, 15642-42-9; difluorosilylene, 13966-66-0; vinyl bromide, 593-60-2.

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