

actinometer for which a quantum yield of 0.38 was used²² giving a reproducible lamp output of 2.01×10^{16} quanta sec^{-1} . After irradiation, the degree of reaction was determined by quantitative vapor phase chromatography. The conversions were run to 10% or less. Octadecane and *p*-phenylbenzophenone were used as internal standards.

Quenching and Sensitization Studies. Solutions of the Δ^3 -oxazolin-5-one (or arylazirine) and dipolarophile containing excess piperylene as a standard triplet quencher were irradiated under conditions where more than 98% of the light was absorbed by the Δ^3 -oxazolinone (or azirine). The reaction was monitored by glpc and in no case was the amount of adduct formed affected by the piperylene. The quencher was present in concentrations sufficiently high to suppress established triplet process.^{19, 20}

Sensitization experiments utilized xanthone as a standard triplet sensitizer. The concentrations were adjusted so that xanthone absorbed greater than 98% of the light. The reaction was monitored by glpc and under the conditions employed; there was no significant cycloaddition detected from the Δ^3 -oxazolinone (or azirine) system with methylacrylonitrile.

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Conformational Analysis. XIX. Silacyclohexanes^{1,2}

Robert J. Ouellette

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. Received March 23, 1973

Abstract: The structure and steric energies of silacyclohexane and the various methylsilacyclohexanes have been calculated by force field methods. Silacyclohexane is predicted to exist in a modified chair conformation in which the ring is more flattened than cyclohexane in the region of silicon and is more puckered in the region of C₄. The 2-, 3-, and 4-methylsilacyclohexanes are calculated to be 1.87, 1.66, and 1.27 kcal/mol, respectively, more stable in the equatorial conformation than in the axial conformation. However, 1-methylsilacyclohexane is predicted to be more stable in the axial conformation by 0.20 kcal/mol. The preference of the 1-methyl group for the axial position is due to a larger negative nonbonded energy term for the axial conformation. Conformational homogeneity of silacyclohexane derivatives could be achieved by the presence of a *tert*-butyl group at the 3 or 4 position as the calculated steric energy differences between equatorial and axial conformations are 4.85 and 6.69 kcal/mol, respectively. 1-*tert*-Butylsilacyclohexane is more stable in the equatorial conformation by only 1.28 kcal/mol. Therefore, *cis*-4-methyl-1-*tert*-butylsilacyclohexane is predicted to be most stable in the conformation with the *tert*-butyl group axial and the methyl group equatorial. *cis*-3,5-Dimethylsilacyclohexane is predicted to be conformationally homogeneous in the diequatorial conformation. The steric energies of four transition states and two skew-boat conformations which may be involved in the ring inversion of 1,1-dimethylsilacyclohexane are calculated. The energies of three of the four possible transition states are consistent with the experimental activation energy obtained by other workers. The structure and steric energies of 3-silabicyclo[3.2.1]octane as well as the 3-methyl and 3,3-dimethyl derivatives are calculated.

Conformations of heterocyclic compounds are affected by many more molecular variables than those of carbocyclic compounds.³ The differences in bond lengths and angles as well as the force constants for bond stretching and bond angle bending make any conformational analogy between heterocycles and carbocycles a tenuous one at best. The change in molecular geometry from that of carbocycles gives rise to subtle changes in van der Waals interactions. Furthermore, heterocycles containing nitrogen⁴ and oxygen⁵ have lone pairs of electrons which may affect conformation.

Heterocycles containing the third row elements phosphorus⁶ and sulfur⁷ have been discussed in the liter-

ature. The proton on phosphorus in phosphacyclohexane prefers the axial position⁸ as does that in protonated thiacyclohexane.⁹ These cases are complicated both by the presence of lone pairs of electrons and by serious deviation, around phosphorus and sulfur, from tetrahedral geometry. We therefore decided to investigate by force field calculation methods the case of a heterocycle containing a third row element not affected by these types of difficulties, namely silacyclohexane. Silacyclohexane should serve as a reference point for the discussion of the conformation properties of other heterocycles containing third row elements.

It has recently been established that force field calculations allow ready prediction of the conforma-

(1) Conformational Analysis. XVIII: R. J. Ouellette, *J. Amer. Chem. Soc.*, **94**, 7674 (1972).

(2) This research was supported by NSF Grant GP 33423. The authors acknowledge the computer time allotted for these calculations from The Ohio State University Computer Center.

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tional energies of organosilanes.^{10,11} The long C–Si bond length and the small torsional barrier about the bond lead to substantial differences in the conformational properties of the silanes and the analogous hydrocarbons. The known torsional barriers for low molecular weight silanes and the conformational energies determined by nmr analysis of the vicinal coupling constants¹¹ in these compounds are in good agreement with the values predicted by force field calculations. The stability of gauche 2-silabutane over that of anti-2-silabutane which is in marked contrast with the opposite order for butane was quantitatively interpreted in terms of the predominant effect of attractive van der Waals terms in 2-silabutane. The significance of the placement of silicon in the chain of atoms was illustrated by the observation that anti-1-silabutane is more stable than gauche 1-silabutane.

Force field calculations involving silicon, germanium, and tin¹² allow for predictions of physical properties of some low molecular weight group IV noncyclic organometallic compounds. These calculations have been successful in providing a rationale for chemical reactions as well.¹³ Therefore force field calculations of heterocyclic compounds of group IV elements could be useful in establishing guideposts to experimental approaches.

Recently substituted silacyclohexanes have been used to study the stereochemistry of reactions at silicon.¹⁴ Stereochemical studies using silacyclohexanes involve geometrical isomers whereas the 1-naphthylphenylmethylsilyl derivatives¹⁵ which have been widely used involve chirality. The silacyclohexanes are potentially experimentally more advantageous for stereochemical studies and of considerably simpler structure.

The purpose of this paper is to provide insights into the structural features of silacyclohexanes which may be important in developing experimental approaches and interpreting data. The calculated steric energies provide predictions about both conformational equilibria and isomerization reactions. Experimental tests are suggested from these calculations. No attempt has been made to estimate the heats of formation of the silacyclohexanes. Only a few values for noncyclic silanes have been experimentally determined and these are highly suspect due to difficulties in achieving complete combustion in the calorimeter. A few heats of formation have been calculated by Allinger.¹⁰

Force Field Calculations. The classical model used in this study involves the calculation of the steric energy, E_s , of the conformation which is defined as the sum of energy terms given in eq 1. The individual terms are

$$E_s = E_r + E_\theta + E_\phi + E_{nb} \quad (1)$$

the energies associated with bond stretching, bond angle deformations, bond torsions, and nonbonded interactions. The force field can be viewed as two harmonic potentials involving bonded atoms and two

nonbonded potentials. The harmonic potentials are given in eq 2 and 3. For each bond or bond angle, the

$$E_r = \sum 1/2 k_r (l - l_0)^2 \quad (2)$$

$$E_\theta = \sum 1/2 k_\theta (\theta - \theta_0)^2 \quad (3)$$

l_0 and θ_0 values are selected to represent "strain free" values. The individual force constants k_r and k_θ are calculated or estimated from normal coordinate analysis of the infrared and Raman spectra of representative molecules.

The torsional potential is given in eq 4 for the three-fold barrier involved in the molecules of interest. The dihedral angle is given by ϕ and the barrier height by k_ϕ .

$$E_\phi = \sum 1/2 k_\phi (1 + \cos 3\phi) \quad (4)$$

The Hill function given in eq 5 is used to account for the attractive and repulsive van der Waals forces.

$$E_{nb} = \sum \epsilon \{ -2.25\alpha^{-6} + 8.28 \times 10^5 \exp(-\alpha/0.0736) \} \quad (5)$$

Energy minimization was achieved by utilizing the method of Boyd.¹⁶ When the root-mean-square deviation of the atomic coordinate positions was less than 0.002 Å the iterative process was terminated.

Details of the modified computer program employed and the identity of the parameters have been given in previous papers.^{11,12}

Structure of Silacyclohexanes. The calculated bond lengths, bond angles, and torsional angles for silacyclohexane and the 1,1-dimethyl, 1(e)-methyl, 1(a)-methyl, 4(e)-methyl, and 4(a)-methyl derivatives are given in Table I. Both the silicon-carbon and carbon-carbon

Table I. Structure of Silacyclohexanes

	Substituents					
	None	1,1-Dimethyl	1(e)-Methyl	1(a)-Methyl	4(e)-Methyl	4(a)-Methyl
$r_{1,2}^a$	1.864	1.863	1.863	1.864	1.862	1.864
$r_{2,3}$	1.531	1.531	1.531	1.531	1.531	1.532
$r_{3,4}$	1.536	1.535	1.536	1.535	1.538	1.541
θ_1^b	104.2	104.4	104.2	104.3	103.8	105.5
θ_2	111.6	111.9	111.6	111.8	111.7	111.9
θ_3	112.5	112.5	112.5	112.5	113.0	114.5
θ_4	113.5	113.5	113.5	113.5	112.6	114.5
$\phi_{1,2}^c$	43.8	42.8	43.7	42.9	44.1	40.5
$\phi_{2,3}$	56.0	55.5	55.9	55.5	56.5	53.4
$\phi_{3,4}$	64.6	64.8	64.6	64.8	63.5	62.0

^a The subscript refers to the atoms bonded; distance in Å.

^b The subscript refers to the central atom of the bond angle; angles in degrees. ^c The subscript refers to the two atoms in the torsional bond; angles in degrees.

bond angles are accepted normal values with only insignificant changes as a function of structure. The bond angles provide interesting structural information; starting from silicon and proceeding around the ring the bond angles increase. The bond angle C–Si–C is significantly less than the tetrahedral angle reflecting the lower force constants involved in bending an angle about silicon. While θ_2 is comparable to the bond angle in cyclohexane, both θ_3 and θ_4 are larger. Allinger's calculations yield 105.5, 107.7, 113.0, and 114.8 for θ_1 through θ_4 , respectively, for the parent compound

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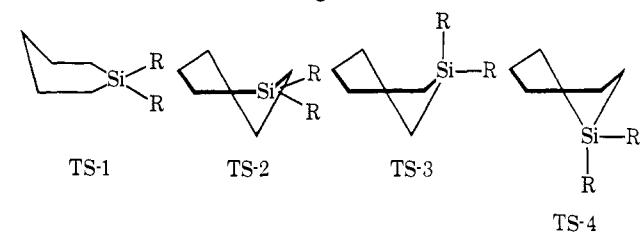
silacyclohexane. Our values differ most significantly for θ_2 . While all features of the force field do interact in a complex manner, significant control of bond angles results from the value of k_θ and θ_0 . Our values are 112.0° and 0.684 mdyne/rad² for C–C–Si. Allinger's values for C–C–Si are not listed but those for C–C–C of 110.2° and 0.40 mdyne/rad² given in an earlier paper¹⁷ were most probably used. In both force fields the θ_2 decreased below the selected natural bond angle. The decrease is more substantial in Allinger's model because of the lower force constant. When structural data on silacyclohexane or compounds such as 1-silapropene become available, the quality of the force fields may be evaluated. Coupled with the bond angle difference relative to cyclohexane, there are significant dihedral angle deviations from 60° . The silacyclohexane ring is flattened in the region of silicon and is an enhanced chair in the region of C₄. No dihedral angles are given by Allinger.¹⁰

Of the compounds listed in Table I, the most significant deviation from an "average" silacyclohexane ring is for the 4(a)-methyl derivative. The 1(a)-methyl derivative exhibits less deviation from the "average." The significance of this observation becomes clear when the conformational preferences of the methyl group are discussed.

It should be noted at this point that all of the compounds listed in Table I are of C_{2v} symmetry. The computer program employed generates these symmetrical structures without explicit symmetry conditions. In all cases the initial coordinates were deliberately chosen to yield an asymmetric molecule. The calculated differences between equivalent features of a molecule are in the next significant figure beyond that reported in Table I.

Transition-State Energies. Unfortunately since no experimental structural data or conformation equilibrium constants for silacyclohexane and its derivatives are available, it is possible to compare the calculated and experimental quantities only for the transition energy of ring reversal. Four possible transition states are illustrated in Chart I. TS-1 has five ring atoms

Chart I. Transition-State Energies



R = H	7.33 (5.42)				
R = CH ₃	4.25 (5.49)	3.83 (5.07)	4.77 (6.01)	10.41 (11.65)	
R = CH ₃ ^a		5.44 (5.46)	5.90 (5.92)	11.31 (11.33)	

^a Calculated by Allinger.¹⁰

coplanar whereas the other three transition states have only four ring atoms coplanar. The calculated steric energies are listed along with the energy difference relative to the chair conformation which are given in parentheses. The predictions of Allinger¹⁰ are also

(17) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Amer. Chem. Soc.*, **93**, 1637 (1971).

given in Chart I. His steric energies average 1 kcal/mol higher than ours but his activation energies are in a general agreement with ours.

Only TS-4 can be disregarded as a potential transition state. As indicated by the component energies listed in Table II, there is severe bond angle strain in

Table II. Transition-State and Skew-Boat Energies of Silacyclohexanes^a

Substituent	Con-formation	E_t	E_{nb}	E_θ	E_ϕ	E_s
None	Chair	0.61	-0.96	1.74	0.51	1.91
None	TS-1	0.58	0.51	1.95	4.29	7.33
1,1-Dimethyl	Chair	0.61	-4.24	1.77	0.63	-1.24
1,1-Dimethyl	TS-1	0.56	-2.78	2.17	4.31	4.25
1,1-Dimethyl	TS-2	0.58	-2.82	2.08	3.99	3.83
1,1-Dimethyl	TS-3	0.73	-2.33	2.41	3.97	4.77
1,1-Dimethyl	TS-4	1.40	-1.74	8.57	2.18	10.41
1,1-Dimethyl	B-1	0.82	-2.96	2.64	3.25	3.74
1,1-Dimethyl	B-2	0.77	-2.77	2.48	2.65	3.13

^a All energies in kcal/mol.

this transition state. Any of the remaining transition states could be regarded as consistent with the activation energy of 5.9 ± 0.3 kcal/mol¹⁸ determined by line-shape analysis of the low temperature nmr of the 1,1-dimethylsilacyclohexane. The calculations are suggestive of multiple transition states leading to a series of skew-boats which may interconvert to ultimately achieve ring reversal.

There appears to be little effect on the transition-state energy due to attached alkyl groups at silicon. Therefore, the experimental and calculated activation energies point to an average value of 5.5 kcal/mol for ring reversal.

Skew-Boat Conformations. Two skew-boat conformations of 1,1-dimethylsilacyclohexane were examined and their energies are given in Table II. They were generated by starting from the two nonequivalent idealized boat conformations. The C_{2v} boat conformation in which the silicon is at the prow is converted to a twist-boat designated B-1. The second twist-boat was generated from the boat conformation in which silicon occupies a gunnel position, and is designated B-2. Both boat conformations are of lower energy than any of the transition states but the difference is very small. This prediction is in marked contrast to cyclohexane which has a transition-state energy twice that of the skew-boat conformation. Thus once the transition state of silacyclohexane is attained a series of skew-boats probably lie at slightly lower energy and are easily interconverted.

Examination of models reveals that TS-2 leads to B-1 whereas TS-3 leads to B-2. In the former case a decrease in energy of 0.7 kcal/mol is predicted whereas in the latter case a decrease of 1.0 kcal/mol is expected.

Since the skew-boat conformations are approximately 4.5 kcal/mol higher in energy than the chair conformation, it would not be expected that the boat conformation would contribute significantly to conformation equilibria. However, since both the barrier energy and the energy difference between skew-boat and chair conformations are smaller than for cyclohexane, it is pos-

(18) C. H. Bushweller, J. W. O'Neal, and H. S. Bilofsky, *Tetrahedron*, **27**, 3065 (1971).

sible for chemical reactions to proceed *via* skew-boat conformations.

Conformational Preference of Methyl. The conformational preferences of a methyl group at the 1, 2, 3, and 4 positions of silacyclohexane may be calculated from the steric energies of the equatorial and axial conformers of the four isomeric compounds. In the cases of the 2-, 3-, and 4-methyl compounds the methyl group prefers the equatorial position. The conformational energies are 1.27, 1.66, and 1.87 kcal/mol, respectively, for the 2-, 3-, and 4-methyl compounds. The nonidentity of the calculated conformational preferences reflects in part the variety of distances separating the axial substituent and the axial hydrogens. In silacyclohexane, the axial hydrogen-hydrogen distances between the hydrogens bonded to the indicated pairs of ring atoms are given by (1,3) = 3.10 Å, (2,4) = 2.57 Å, (2,6) = 3.16 Å, and (3,5) = 2.54 Å.

1-Methylsilacyclohexane is predicted to be more stable in the axial conformation and the conformational preference is -0.2 kcal/mol. Allinger¹⁰ predicts the same order of stability but the energy difference is -0.06 kcal/mol. In the axial conformation two *gauche* 2-silabutane interactions occur whereas in the equatorial conformation two *anti*-2-silabutane interactions occur. As illustrated in earlier work, the *gauche* conformation of 2-silabutane is more stable than the *anti* conformation which is the reverse of the order found in butane.

Examination of the component energies given in Table III for the pairs of conformers of the isomeric

Table III. Conformational Energies of Methylsilacyclohexanes^a

Position	E_r	E_{nb}	E_θ	E_ϕ	E_s
1(e)	0.61	-2.33	1.73	0.53	0.54
1(a)	0.60	-2.61	1.73	0.62	0.34
2(e)	0.77	-0.96	2.06	0.48	2.35
2(a)	0.90	-0.60	2.66	0.67	3.62
3(e)	0.79	-1.77	1.84	0.55	1.40
3(a)	0.93	-1.43	2.85	0.71	3.06
4(e)	0.82	-1.73	1.98	0.53	1.61
4(a)	0.96	-1.11	2.86	0.77	3.48

^a Energies in kcal/mol.

methylsilacyclohexanes reveals the reason for the unusual stability of 1(a)-methylsilacyclohexane. For each of the other three pairs of compounds, slight increases in E_r and E_ϕ occur in the axial conformation over the equatorial conformation. However, the most significant change is a decrease in the overall attractive character of E_{nb} and a large increase in E_θ for the axial conformation. For the 1(a)-methylsilacyclohexane the E_r and E_θ terms change less than for the other isomers. In addition E_θ does not change at all and E_{nb} indicates increased attractive character. Thus, while the axial conformers of the 2-, 3-, and 4-methyl isomers involve structural distortions to move the axial methyl group away from the other axial hydrogens, the 1-methyl group finds a favorable total attractive position in the axial conformation.

***tert*-Butylsilacyclohexanes.** The *tert*-butyl group is one of the classical groups used to "lock" cyclohexane derivatives or more specifically a means of achieving near-conformational homogeneity. Therefore, the energies of the equatorial and axial conformations of three

of the four isomeric *tert*-butylsilacyclohexanes were calculated.

For each of the conformations examined the component and total steric energies are given in Table IV

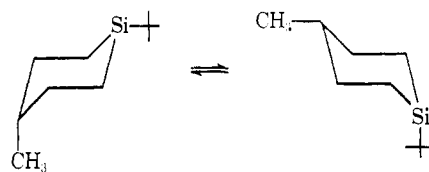
Table IV. Conformational Energies of *tert*-Butylsilacyclohexanes

Substituent	E_r	E_{nb}	E_θ	E_ϕ	E_s
4(e)	2.63	-1.13	5.17	1.40	8.08
4(a)	3.04	-0.16	9.68	2.20	14.77
3(e)	2.51	-1.38	5.39	0.96	7.47
3(a)	2.73	-0.92	8.61	1.90	12.32
1(e)	1.50	-2.38	3.10	0.41	2.63
1(a)	1.55	-2.70	3.57	1.49	3.91
<i>cis</i> -4-Methyl-1(a)	1.76	-3.53	3.82	1.51	3.55
<i>cis</i> -4-Methyl-1(e)	1.83	-2.78	4.13	0.75	3.94

The conformational preferences for the equatorial positions of the 3- and 4-*tert*-butyl groups are 4.85 and 6.69 kcal/mol, respectively. Clearly, the *tert*-butyl group in either position would ensure conformational homogeneity for compounds substituted at silicon and at either the 3 or 4 position. The order of the conformational energies of the *tert*-butyl group parallels that of the methyl group at similar positions.

The conformational preferences of the 1-*tert*-butyl group is for the equatorial position. The increased degree of substitution over that of a methyl group changes the conformational energy difference from -0.20 for methyl to +1.28 kcal/mol for *tert*-butyl. However, the change is far less than for the other ring positions of silacyclohexane or cyclohexane.

An interesting conformational prediction concerning the populations of *cis*-4-methyl-1-*tert*-butylsilacyclohexane can be made. Assuming that the conformational preferences are additive, the conformation in which the *tert*-butyl group is axial is predicted to be more stable than the alternate conformation by 0.59 kcal/mol. Therefore even a sterically bulky group attached to silicon will not ensure conformational homogeneity. Calculations of the energies of both con-



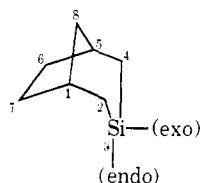
formations yield the results given in Table IV. The calculated energy difference between the two conformations is 0.39 kcal/mol.

3,5-Dimethylsilacyclohexanes. An alternative way to ensure conformational homogeneity in cyclohexane derivatives involves the use of *cis*-3,5-dimethyl-substituted compounds. While the conformational preference of a single methyl group is relatively small, the presence of *cis*-methyl groups in the 3 and 5 positions should raise the energy of the diaxial conformation. Accordingly, calculations for 3,5-dimethylsilacyclohexane were carried out. The results given in Table V clearly show that the diequatorial conformation is favored over the diaxial conformation by 6.19 kcal/mol. In terms of synthetic approaches to conformationally homogeneous silacyclohexanes, the *cis*-3,5-dimethyl-substituted compounds are more accessible than the singly substituted *tert*-butyl derivatives.

Table V. 3,5-Dimethylsilacyclohexane

Conformation	E_r	E_{nb}	E_θ	E_ϕ	E_s
Diequatorial	0.97	-2.59	1.92	0.59	0.89
Diaxial	1.41	-1.34	5.48	1.53	7.08

3-Silabicyclo[3.2.1]octane contains a silacyclohexane bridged by a bimethylene bridge across the 3 and 5



positions. The molecule provides a potentially attractive means of studying reactions at the silicon center. Products fall in the class of geometrical isomers and should be readily separable by a variety of chromatographic means. The bond lengths, bond angles, and torsional angles of the parent compound and the 3,3-dimethyl, *exo*-3-methyl, and *endo*-3-methyl derivatives are given in Table VI. There are some slight differences

Table VI. Structure of 3-Silabicyclo[3.2.1]octanes

	Substituents			
	None	3(e)-Methyl	3,3-Dimethyl	3(a)-Methyl
$r_{1,2}^a$	1.534	1.534	1.534	1.533
$r_{2,3}$	1.869	1.868	1.870	1.870
$r_{5,6}$	1.531	1.531	1.530	1.530
$r_{1,8}$	1.524	1.524	1.523	1.524
$r_{6,7}$	1.536	1.536	1.535	1.535
$\theta_{1,2,3}^b$	112.4	112.4	113.4	113.3
$\theta_{2,3,4}$	105.6	105.7	106.6	106.5
$\theta_{2,1,8}$	111.0	111.0	110.9	111.1
$\theta_{2,1,7}$	112.3	112.3	112.5	112.4
$\theta_{8,1,7}$	103.2	103.2	103.4	103.3
$\theta_{1,8,5}$	103.8	103.8	103.8	103.8
$\theta_{1,7,6}$	106.4	106.4	106.4	106.4
$\phi_{1,8,5,6}^c$	39.7	39.7	39.4	39.4
$\phi_{1,5,6,7}$	24.2	24.1	24.0	24.3
$\phi_{3,4,5,6}$	59.5	59.6	64.5	63.9
$\phi_{1,7,6,5}$	0.1	0.1	0.2	0.2
$\phi_{1,2,3,4}$	32.0	32.0	22.0	21.5
$\phi_{2,1,8,5}$	78.7	78.7	79.3	79.5

^a Subscript refers to bonded atoms; distance in Å. ^b Subscript refers to order of bond atoms; angle in degrees. ^c Subscript refers to order of atoms torsionally bonded; angles in degrees.

in the bond length of 3-silabicyclo[3.2.1]octane compared to silacyclohexane, but the most significant change is a 0.01 Å shortening of the C₁-C₃ bond compared to the C₃-C₄ bond angle of silacyclohexane. The C-Si-C bond angle of 3-silabicyclo[3.2.1]octane is expanded by 1.4° but the C₁-C₃-C₅ bond angle is compressed by 8.7° compared to silacyclohexane. Both of these changes reflect necessary structural compromises to bridge the 3 and 5 axial positions of silacyclohexane. A substantial torsional change about the C-Si-C-C portion of the molecule occurs. The torsional angle decreases from approximately 43° in silacyclohexane to 32° in 3-silabicyclo[3.2.1]octane and the *exo*-3-methyl derivative. In addition, the presence of an axial methyl group in

both the 3,3-dimethyl and *endo*-3-methyl compounds causes a further change to 22°. Thus the C-Si-C flap of the chair is flattened somewhat as a result of the bimethylene bridge and this flattening is further enhanced by the presence of 3(a)-methyl groups.

The calculated steric energies of the 3-silabicyclo[3.2.1]octanes examined are given in Table VII. The

Table VII. Energies of 3-Silabicyclo[3.2.1]octanes^a

Substituent	Conformation	E_r	E_{nb}	E_θ	E_ϕ	E_s
None	Chair	0.82	-0.33	4.94	5.15	10.58
None	Transition	0.84	0.88	5.04	7.50	14.26
None	Skew-boat	1.04	1.86	6.99	7.07	16.93
3(e)-Methyl	Chair	0.82	-1.75	4.91	5.17	9.16
3(a)-Methyl	Chair	0.79	-1.91	4.94	5.94	9.76
3,3-Dimethyl	Chair	0.78	-3.66	5.04	5.96	8.12

^a Energies in kcal/mol.

exo-3-methyl compound is 0.6 kcal/mol more stable than the *endo*-3-methyl compound. Thus the presence of the bimethylene bridge reverses the conformational preference of an axial methyl group calculated for silacyclohexane. However, the extent of the destabilization is only 0.8 kcal/mol. In bicyclo[3.2.1]octane the calculated energy difference between the *exo*- and *endo*-3-methyl compounds is 5.23 kcal/mol!¹⁹ This latter calculated energy difference is consistent with experimental observations.^{19,20} The longer C-Si bonds in 3-silabicyclo[3.2.1]octanes decrease the severity of van der Waals repulsions between the 3 position and the bimethylene bridge.

A planar transition state in which the silicon atom moves up into the plane defined by carbon atoms 1, 2, 4, and 5 was assumed to be a reasonable one for conversion to a boat conformation for 3-silabicyclo[3.2.1]octane. The barrier is only 3.68 kcal/mol and is approximately 1.7 kcal/mol less than for silacyclohexane. This decrease in energy reflects the flattening of the chair conformation in the vicinity of silicon. Furthermore, the bridging bimethylene unit spreads apart the molecule in the vicinity of silicon and allows for development of the transition state with a smaller increase in energy. A skew-boat generated by the computer is 6.35 kcal/mol above the chair conformation. The analogous boat for silacyclohexane is 4.98 kcal/mol above the chair conformation. The bimethylene bridge restricts those torsional changes which allow for achievement of a relatively low energy skew-boat conformation in silacyclohexane.

The silabicyclo[3.2.1]octane ring appears to be an attractive one for stereochemical studies. Both the low strain energy of the chair conformation and the low population of the boat conformation are suggestive of a conformationally homogeneous system. In addition, substituents at silicon are easily accommodated in either the *exo* or *endo* position.

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(19) D. Rawn and D. Baron, unpublished experimental data and calculations.

(20) N. A. Belikovo, A. A. Bobyleva, and A. F. Platé, *Zh. Org. Khim.*, 4, 424 (1968).