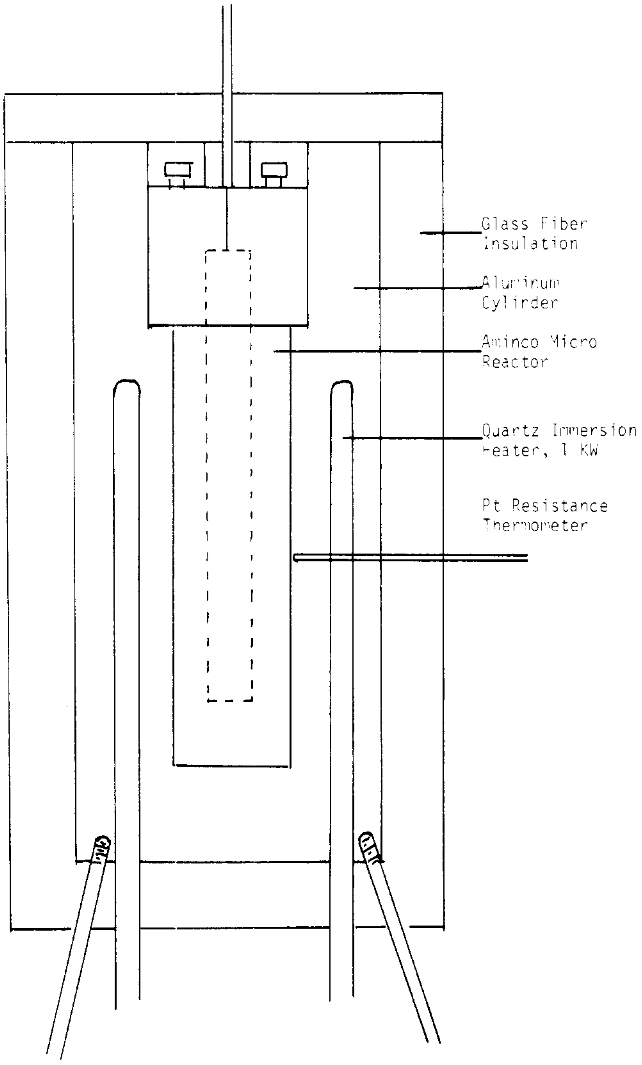

Figure 5. Apparatus used to heat pressure vessel.

compressibility. The time of attainment of the control temperature is noted and converted to an equivalent starting time as described below. Pressure adjustments are made during the next 0.5 h. After a suitable time (1 h minimum) the reactor is lifted clear of the thermostat and cooled at an initial rate of 15 °C/min (from 400 °C) by a blower. Throughout the cooling period the pressure is maintained at 6.7 MPa or higher by pumping. When the cell has been removed from the reactor, the plunger can easily be pulled out against atmospheric pressure.

Determination of the Equivalent Starting Time. After the thermostat has reached the control temperature, the inner temperature of the reactor can be monitored by means of the pressure rise by using measured values of $(\partial T/\partial P)_V$. For our apparatus the derivative has values of 3.7 and 2.1 °C/MPa at 350 and 260 °C, respectively. It has been found that the rate of change of temperature with time is given by eq 1 in which T' is the control

$$\frac{T'-T}{T'-T_0} = e^{-kt} \qquad (1)$$

temperature and T_0 is the temperature when $t = 0$. Substitution in the Arrhenius equation gives the ratio, Q, of the rate constants at T and T' as shown in eq 2. The equivalent starting time, t_0,

$$Q = \exp\left[\frac{E_{act}}{R}\left(\frac{1}{T'} - \frac{1}{T'-(T'-T_0)e^{-kt}}\right)\right] \qquad (2)$$

is defined by eq 3. The amount of reaction which has occurred

$$\int_0^{t_0} Q \, dt = \int_{t_0}^{\infty} (1-Q) \, dt \qquad (3)$$

before t_0 is set equal to the deficiency of reaction beyond t_0, and thus the amount of reaction at time t is the same as though the reaction had reached T' at t_0. It is always possible to make the reaction slow enough to justify the assumption that only a small percentage of reaction has occurred up to about $2t_0$. For the thermolysis of bibenzyl at 400 °C the values of the constants are $T_0 = 320$ °C, $k = 1.5 \times 10^{-3}$ s^{-1}, and $E_{act} = 63$ kcal. Figure 4 gives Q as a function of t in minutes. The equated integrals of preceding eq 3 are represented by the shaded areas. The probable error in t_0 is about 1 min. We therefore use minimum reaction times of 1 h.

Thermostat. The pressure vessel is heated by the apparatus shown in Figure 5. Two pairs of 1-kW quartz heaters are wired in series to provide 4-kW at 230 V and 1-kW at 115 V. It is also possible to disconnect one pair to provide control heat at 0.5 kW. At 400 °C the power dissipation is about 0.35 kW. The reactor is lowered into the cavity by means of a coil of flexible pressure tubing, and the assembly is brought up to control temperature at 7–8 °C/min. The bandwidth of the controller is ±1 °C. Temperature variations within the reactor can be followed by the pressure guage. Throughout one cycle of the controller the temperature change is less than 0.15 °C and over several hours it is not more than 1 °C. Temperatures were calibrated at the melting points of zinc and lead.

Registry No. Bibenzyl, 103-29-7.

Conformational Preference of the Trimethylstannyl Group

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The conformational preference of the trimethylstannyl group in (trimethylstannyl)cyclohexane has been determined through analyses of *cis*- and *trans*-1-methoxy-d_3-4-(trimethylstannyl)cyclohexane by ^{1}H NMR spectroscopy. The chemical shift of the equatorial trimethylstannyl protons has been shown to be upfield of the axial protons. The *A* value for the trimethylstannyl group is 0.94 ± 0.03 kcal/mol. It is demonstrated that the *A* values of the methoxy-d_3 and the trimethylstannyl groups are approximately additive.

A recent report by Kitching[1] and others on the stereochemistry of substitution reactions of the trimethylstannyl anion with cyclohexyl derivatives relied heavily upon ^{13}C chemical shifts and ^{13}C–^{117,119}Sn coupling constants to establish the conformation of reaction products. Some evidence from ^{1}H NMR spectroscopy was also observed, but it was inconclusive. The ^{13}C NMR spectral evidence was interpreted on the basis of previous ^{13}C work done by Kitching[2] in determining the *A* value of the trimethyl-

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[1] W. Kitching, H. Olszowy, J. Waugh, and D. Doddrell, *J. Org. Chem.*, 43, 898 (1978).

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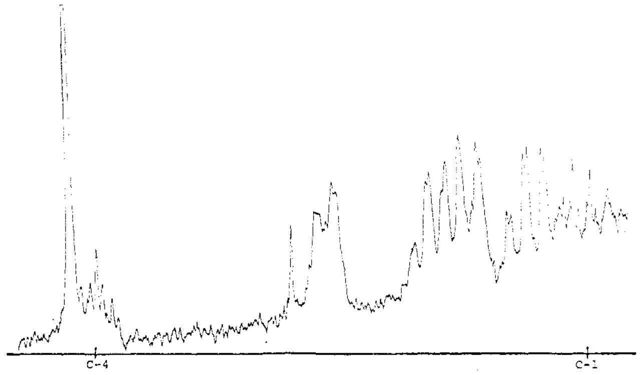


Figure 1. 100-MHz ^{1}H NMR spectrum of the C-1 and C-4 protons of *trans*-(4-methoxycyclohexyl)trimethyltin with shift reagent Eu(thd)$_3$ in CDCl$_3$ (Me$_4$Si reference) at room temperature (50 mg of *trans*-(4-methoxycyclohexyl)trimethyltin, 26 mg of Eu(thd)$_3$, 0.5 mL of CDCl$_3$, 0.2 mL of Me$_4$Si).

stannyl group in (trimethylstannyl)cyclohexane. Although their spectral interpretations left some doubt, their conclusions were correct as shown by the compelling evidence of ^{1}H NMR spectroscopy presented in this paper.

Results and Discussion

Low-temperature[3] (−93 °C) ^{1}H NMR studies of (trimethylstannyl)cyclohexane in carbon disulfide showed separate proton resonances for axial and equatorial trimethylstannyl protons, the larger peak (conjectured to be the equatorial form) being upfield. Determination of the A value ($A = -\Delta G°/1000 = RT \ln K_{eq}/K_{ax}$) by integration of the peak areas showed an energy preference of 0.94 ± 0.03 kcal/mol. The question remained whether this preference was axial or equatorial.

To answer this question, *cis*- and *trans*-4-methoxy-1-(trimethylstannyl)cyclohexane (and their deuterated methoxy derivatives) were prepared and separated by preparative gas chromatography and the protons at C-1 and C-4 in each compound were studied by ^{1}H NMR spectroscopy.[4] Since the OCH$_3$ and OCD$_3$ groups prefer the equatorial position (the A value for OCD$_3$ is 0.547 kcal/mol[5]), the equatorial or axial preference of the trimethylstannyl group will affect $\Delta G°$ in varying ways.

1. If the trimethylstannyl group prefers the equatorial position (A = +0.94 kcal/mol), the additive A values ($-\Delta G°$ = +0.94 kcal/mol + 0.547 kcal/mol = +1.487 kcal/mol) would lock the trans isomer in the diequatorial form and show axial protons in the NMR spectra at C-1 and C-4. The cis isomer would show preference to the equatorial trimethylstannyl group ($-\Delta G°$ = +0.94 kcal/mol − 0.547 kcal/mol = 0.393 kcal/mol) and thus show an axial proton at C-1 and an equatorial proton at C-4 (of course, if the A values are not additive, $-\Delta G°$ may be much different and the C-1 and C-4 proton peaks may not be easily resolved).

2. If the trimethylstannyl group prefers the axial position (A = −0.94 kcal/mol), the cis isomer would be locked [$-\Delta G°$ = +0.547 kcal/mol − (−0.94 kcal/mol) = +1.487 kcal/mol] with the stannyl group axial and the methoxy group equatorial showing an equatorial proton at C-1 and an axial proton at C-4. The trans isomer would show preference to the diaxial form ($-\Delta G°$ = −0.94 kcal/mol + 0.547 kcal/mol = −0.393 kcal/mol) and the protons at C-1 and C-4 would be equatorial.

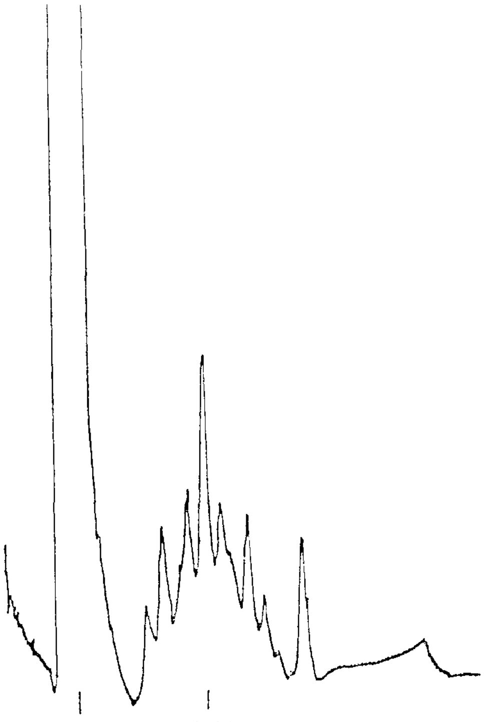
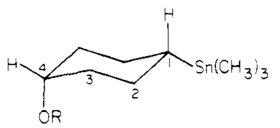
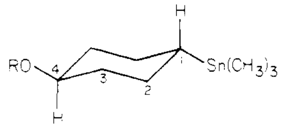


Figure 2. 220-MHz ^{1}H NMR spectrum of the C-4 protons (δ 2.94 downfield from Sn(CH$_3$)$_3$) of 1.20 M *trans*-(4-methoxycyclohexyl)trimethyltin in CS$_2$ at room temperature.

Proton–proton coupling in cyclohexyl systems has been studied extensively. It is well-known that an axial proton at C-1 or C-4 in this system would show a triplet of triplets with a half-width of >20 Hz while an equatorial proton would show a broad singlet with a half-width of 10–15 Hz.[6,7] Identification of the cis (I) and trans (II) isomers by ^{1}H NMR spectroscopy thus proved that the trimethylstannyl group prefers the equatorial position with an A value of +0.94 ± 0.03 kcal/mol.



Ia, R = CD$_3$
b, R = CH$_3$



IIa, R = CD$_3$
b, R = CH$_3$

Compound II was shown conclusively to be the trans isomer by a 100-MHz ^{1}H NMR spectrum with lanthanide shift reagent Eu(thd)$_3$. The spectrum clearly showed a triplet of triplets for both H$_1$ and H$_4$ (Figure 1). It was proven that this configuration was not caused by the Eu(thd)$_3$ shift reagent by observing that the H$_4$ proton resonance was again a triplet of triplets in the absence of the shift reagent (Figure 2). Thus, II was shown conclusively to be trans and the equatorial preference of the trimethylstannyl group was established. Low-temperature studies (−94 °C) of the trans isomer showed only a slight

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(2) (a) W. Kitching, D. Doddrell, and J. B. Grutzner, *J. Organomet. Chem.*, **107**, C5 (1976); (b) R. C. Putnam and H. Pu, *Can. J. Chem.*, **44**, 1343 (1966); (c) H. G. Kuivila, J. L. Considine, R. J. Mynott, and R. H. Sarma, *J. Organomet. Chem.*, **55**, C11 (1973); (d) D. Doddrell, I. Burfitt, W. Kitching, M. Bullpitt, C. H. Lee, R. J. Mynott, J. L. Considine, H. G. Kuivila, and R. H. Sarma, *J. Am. Chem. Soc.*, **96**, 1640 (1974).

(3) A specially constructed low-temperature probe was used as described in F. R. Jensen, L. A. Smith, C. H. Bushweller, and B. H. Beck, *Rev. Sci. Instrum.*, **43**, 894 (1972).

(4) F. R. Jensen and K. C. Hsu, in process of publication.

(5) F. R. Jensen, C. H. Bushweller, and B. H. Beck, *J. Am. Chem. Soc.*, **91**, 344 (1969).

(6) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, 1969, pp 132–40.

(7) F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 1053 (1962).

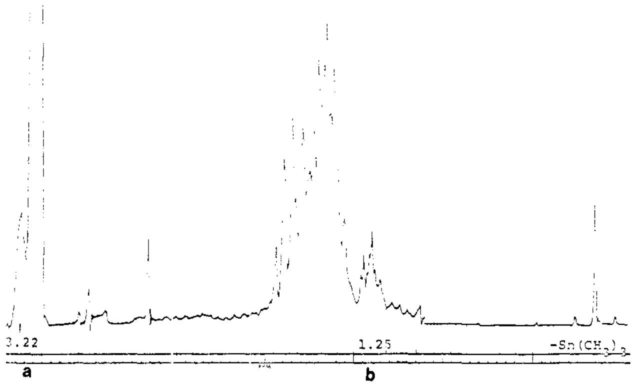

Figure 3. 220-MHz ^{1}H NMR spectrum of 1.20 M *cis*-(4-methoxycyclohexyl)trimethyltin in CS_2 at room temperature: (a) C-4 proton 3.22 ppm downfield of $Sn(CH_3)_3$; (b) C-1 proton 1.25 ppm downfield of $Sn(CH_3)_3$.

upfield shift of the trimethylstannyl hydrogens showing the isomer to exist predominantly in the diequatorial conformation.

Compound I was identified as the cis isomer by 220-MHz ^{1}H NMR sepctroscopy. The C-4 proton showed a broad singlet (>70% axial OCD_3)[6,7] and the C-1 proton showed a triplet of triplets (>70% equatorial $Sn(CH_3)_3$)[6,7] (Figure 3). This evidence shows undoubtedly that the trimethylstannyl group prefers the equatorial position. Low-temperature (-90 °C) 100-MHz ^{1}H NMR studies of the cis isomer showed the trimethylstannyl protons to separate with the larger peak upfield as in (trimethylstannyl)cyclohexane.

Low-temperature ^{1}H NMR studies of the cis and trans isomers yielded further data in support of the reliability of the "additive *A* value" concept. It has been shown that the deuterated methoxy group prefers the equatorial position ($A = 0.547$ kcal/mol).[5] The concept of additive *A* values (in the cis isomer (I), $A_{Sn(CH_3)_3} - A_{OCD_3} = 0.94$ kcal/mol − 0.55 kcal/mol = 0.39 kcal/mol) was tested by determining the $-\Delta G°$ of I through peak area measurement of 100-MHz ^{1}H NMR spectra (-93 °C) for the proton at C-4 and the methyl protons of the stannyl group on C-1. Calculation for the proton at C-4 gave $-\Delta G° = -0.44 \pm 0.02$ kcal/mol, while measurement of the stannyl group proton peaks gave $-\Delta G° = -0.46 \pm 0.03$ kcal/mol. A comparison of the calculated and experimental results shows fairly good agreement.

The only noticeable change when the trans isomer (II) was cooled to -94 °C was an upfield shift of 2.3 Hz for the axial proton at C-4. No separation into axial and equatorial peaks was observed for either the hydrogen on C-4 or the hydrogens of the stannyl group at C-1. On the basis of the maximum separation of the equatorial and axial protons on C-4 observed in I (48.3 Hz), the $-\Delta G°$ for the trans isomer is 1.8 kcal/mol. In this case, the percentage difference between additive *A* value ($A_{Sn(CH_3)_3} + A_{OCD_3} =$ 0.94 kcal/mol + 0.55 kcal/mol = 1.49 kcal/mol) and the experimental $-\Delta G°$ (1.8 kcal/mol) is about the same as that for the cis isomer.

These studies offer conclusive evidence that the trimethylstannyl group prefers the equatorial position in cyclohexyl systems and show that the conclusions drawn by Kitching[1] and others are valid, thus giving more credibility to the use of ^{13}C chemical shifts and $^{117,119}Sn-^{13}C$ coupling constants in the conformational and stereochemical analysis of cyclohexyl systems.

Experimental Part

All spectra were recorded in CS_2, with the tin methyl hydrogens used as a lock signal when necessary, on a Varian HA-100 spectrometer utilizing a specially constructed probe.[3] Spectra used for peak area measurements were run in the HR operating mode. The movement of the C-4 proton in II was studied with and without a Me_4Si lock signal and gave similar results.

Physical Properties of Trimethyltin Compounds.[2a] ***cis*-(4-Methoxycyclohexyl)trimethyltin**: IR (film, neat) 3.36 (m), 3.44 (s), 3.51 (m), 6.90 (m), 6.96 (m), 7.32 (m), 7.39 (w), 7.45 (w), 7.88 (w), 8.02 (w), 8.35 (w), 8.45 (w), 8.52 (w), 8.69 (w), 9.05 (s), 9.15 (s), 9.80 (w), 10.00 (m), 13.15 (s) μm; ^{1}H NMR (60 MHz, $CDCl_3$) [$(CH_3)_3Sn$ is δ 7.26 upfield from the residual protons of $CDCl_3$] δ (relative to $(CH_3)_3Sn$) 0 (s, 9 H), 0.95–2.30 (m, 9 H, centered at δ 1.62), 3.27 (s, 4 H).

***trans*-(4-Methoxycyclohexyl)trimethyltin**: IR (film, neat) 3.36 (m), 3.43 (s), 3.51 (s), 3.55 (m), 6.86 (m), 6.93 (m), 7.32 (w), 7.40 (w), 8.00 (w), 8.30 (m), 8.55 (m), 8.75 (m), 9.00 (s), 10.69 (m), 13.00 (s) μm; ^{1}H NMR (60 MHz, $CDCl_3$) [$(CH_3)_3Sn$ is δ 7.27 upfield from the residual protons of $CDCl_3$] δ (relative to $(CH_3)_3Sn$) 0 (s, 9 H), 0.76–1.50 (m, 5 H), 1.50–2.36 (m, 4 H), 2.87–3.20 (m, 1 H, centered at δ 3.04), 3.30 (s, 3 H).

***cis*-(4-Methoxy-d_3-cyclohexyl)trimethyltin**: IR (film, neat) 3.35 (w), 3.42 (s), 3.50 (s), 4.57 (w), 4.86 (m), 6.93 (w), 6.96 (w), 7.34 (w), 7.89 (w), 8.08 (w), 8.50 (w), 8.71 (w), 8.75 (s), 9.10 (w), 9.30 (m), 9.59 (w), 10.15 (w), 11.25 (w), 13.18 (s), 15.08 (m) μm; ^{1}H NMR (60 MHz, CS_2) δ (relative to $(CH_3)_3Sn$) 0 (s, 9 H), 0.73–2.60 (m, 9 H), 3.21 (m, 1 H).

***trans*-(4-Methoxy-d_3-cyclohexyl)trimethyltin**: IR (film, neat) 3.40 (m), 3.45 (s), 3.55 (s), 4.89 (m), 6.92 (m), 8.84 (s), 9.00 (s), 9.40 (w), 9.45 (w), 9.85 (w), 10.10 (w), 10.21 (w), 11.10 (w), 13.10 (s), 14.10 (w), 15.10 (w) μm; ^{1}H NMR (60 MHz, CS_2) δ (relative to $(CH_3)_3Sn$) 0 (s, 9 H), 0.68–1.53 (m, 4 H), 1.53–2.30 (m, 4 H), 2.95 (m, 1 H).

Acknowledgment. This work was supported by grants from the National Science Foundation (Grant GP-33669) and the National Institutes of Health (Grant GM-15373).

Registry No. Ib, 72659-39-3; IIb, 72659-40-6.