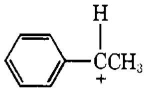
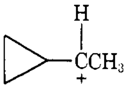
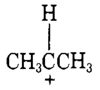
cyclopropyl substituents by their ability to delocalize positive charge. The reported carbonium ion carbon chemical shifts of ions **6** and **7** are also shown for comparison in Table II.



1-H



6



$$CH_3\overset{H}{\underset{+}{C}}CH_3$$

7

The ability of the phenyl groups to delocalize positive charge, from the values of ^{13}C chemical shifts in the ions compared followed the expected sequence $p\text{-}CH_3OC_6H_4 > [2,4,6\text{-}(CH_3)_3]C_6H_2\text{-} > p\text{-}CH_3C_6H_4 > C_6H_5 > p\text{-}CF_3C_6H_4$. The effect on ^{13}C chemical shift replacement of hydrogen in a secondary carbonium ion at the carbonium ion carbon by a methyl group is similar for all three types (phenyl, cyclopropyl, methyl) of substituents compared. The effect is greatest with cyclopropyl, and least with methyl substituents. It should be emphasized, however, that at this point we are comparing systems which place the carbonium carbon atom in different environments. The effect in terms of change of delocalization of these small $\Delta\delta_{^{13}C}$ values is difficult to estimate at the present time, as chemical shifts cannot be correlated with charge densities alone. Methyl groups attached to the carbonium ion center, however, seem consistently to be electron withdrawing compared to hydrogen.[4a]

Experimental Section

Preparation of Ions. The styryl ions were prepared in 3 : 1 v/v solution of $SO_2ClF\text{-}SbF_5$ at −78°. The precursor alcohol is frozen to the inside of the test tube above the surface of the liquid. It is then carefully washed with the ionizing solvent by means of a vortex mixer. In the cases of **1-H** and **1-CF$_3$**, attempts to build up the ion concentration to a high level resulted in polymerization.

2-H and **2-CH$_3$** are commercially available and were used without purification. **2-H** was obtained from K & K Laboratories and **2-CH$_3$** from Aldrich Chemical Co. **2-[2,4,6-(CH$_3$)$_3$]** was described in ref 2.

2-OCH$_3$ was prepared by treating 25 ml of *p*-methoxybenzaldehyde in 50 ml of diethyl ether with 70 ml of 3 *M* methylmagnesium bromide in ether (Arapahoe) at −5°. After addition was completed, they were refluxed 30 min and worked up in the usual way. A 14.8-g sample of **2-OCH$_3$** (47%) was obtained, bp 93.5–95.0 (3.5 mm).

2-CF$_3$ was prepared by addition of acetaldehyde to the Grignard reagent made from 11.2 g of *p*-trifluoromethylbromobenzene and 1.3 g-atoms of magnesium, yield 4.0 g (42%) of **2-CF$_3$**, bp 72° (4 mm). Nmr parameter of all **2-X** precursor alcohols are given in Table III.

Table III. Pmr Parameters[a] for Alcohols **2-X**

	CH_3	CH	ortho	meta	X
2-OCH$_3$	1.28 (6.5)	4.61	7.13	6.69	3.64
2-[2,4,6-(CH$_3$)$_3$]	1.37 (6.7)	5.16	2.31	6.67	2.18
2-CH$_3$	1.26 (6.6)	4.59	7.04	7.04	2.25
2-H	1.25 (6.5)	4.60	7.15	7.15	7.15
2-CF$_3$	1.38 (6.5)	4.79	7.34	7.55	

[a] Chemical shifts relative to TMS in CCl_4. Coupling constants in hertz in parentheses.

Nmr Measurements. Precursor alcohols and styryl cations were run (pmr) on a Varian Associates Model A 56/60 spectrometer. Indor measurements were carried out on a Varian Associates Model HA-100 spectrometer with details described previously.[5] Time averaging was done with a C-1024 time-averaging computer; the method is described in the text.

Acknowledgment. Support of this work by grants from the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

Internal Solvent Pressure. I. A Demonstration of the Effect of Internal Solvent Pressure on Conformational Equilibria[1]

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Abstract: The role of internal solvent pressure in controlling conformational equilibria is discussed. Conformational studies of 4,4-dimethyl-2-silapentane and 2,3-dimethyl-2-silabutane establish that internal solvent pressure increases the population of *gauche*-butane conformations with respect to *trans*-butane conformations. The differences in molar volumes for the trans $\rightleftharpoons$ gauche equilibria −3.7 and −4.1 cm^3/mol for 4,4-dimethyl-2-silapentane and 2,3-dimethyl-2-silabutane, respectively. It is suggested that internal solvent pressure may play a role in controlling equilibria and kinetics of systems in which solvent effects are usually considered negligible.

The terms used to describe the liquid state and its effects in organic chemistry range from measurable thermodynamic properties,[2-6] semiempirical parameters,[7-9] and intuitive qualitative generalizations.

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[1] The authors acknowledge Grant GP-9231 from the National Science Foundation in support of this research.

[2] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, pp 50–55, 147–155, 263–267.

[3] K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, pp 253–272.

[4] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw Hill, New York, N. Y., 1960, pp 504–510.

[5] L. L. Schaleger and F. A. Long, "Advances in Physical Organic Chemistry," Vol. 1, Academic Press, New York, N. Y., 1963, pp 1–31.

[6] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1958, pp 113–146.

[7] J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1962, pp 157–162.

While the number of terms does not exceed the observations which gave rise to their birth, a given experimental fact obtained from a liquid system presents a challenge in interpretation because of the sheer number of models which must be considered. Well-recognized features such as hydrogen bond and dipole–dipole interactions may give rise to large differential solvent effects which are easily ascribable at least in a major part to these phenomena. Often the most difficult observations to explain are those involving small net changes with variation in solvent. One thermodynamically based term which has escaped exploitation in organic chemistry to date is that of internal pressure.[10–12]

A change in internal energy with respect to a change in volume at constant temperature, $(\partial E/\partial V)_T$, is known as the internal pressure and is the result of a balance of attractive and repulsive forces within the liquid state. The work required in overcoming internal pressure in order to create a solvent cavity is given by eq 1. There

$$\left(\frac{\partial E}{\partial V}\right)_T \mathrm{d}V = P_i\mathrm{d}V \qquad (1)$$

are several ways to determine P_i. Equation 2 can be derived from equations of state. For cases where

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \cong T\left(\frac{\partial P}{\partial T}\right)_V \qquad (2)$$

external pressure is small with respect to internal pressure, a determination of $T(\partial P/\partial T)_V$ yields P_i. From definitions of the coefficients of thermal expansion, α, and of compressibility, β, the internal pressure may be calculated by means of eq 3.

$$P_i = T(\alpha/\beta) \qquad (3)$$

An approximate evaluation of internal pressure is obtained by differentiation of the van der Waals gas equation with respect to temperature at constant volume for 1 mol of a gas followed by substitution in eq 2.

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b} \qquad (4)$$

$$\left(\frac{\partial E}{\partial V}\right)_T = P_i = \frac{a}{V^2} \qquad (5)$$

However, since the van der Waals equation is an approximation the term a/V^2 is not an exact measure of P_i. Improved values have been obtained by empirical fits of van der Waals type equations using a/V^{n+1} by varying n.[13] Alternatively k/V^2 has been employed where k is an empirical constant not equal to a.[12]

A third method of determining P_i is based on the assumption that the internal molar latent heat of vaporization is a measure of the work required against the internal pressure in vaporizing 1 mol of liquid occupying a volume V. Hildebrand[14] has shown that

$$L_i \cong \left(\frac{\partial E}{\partial V}\right)_T V \qquad (6)$$

$$P_i = \left(\frac{\partial E}{\partial V}\right)_T \cong \frac{L_i}{V} \qquad (7)$$

at ordinary temperatures the latent heat of vaporization is given by eq 8, where T_b is the normal boiling point on the absolute scale. Therefore internal pressures may

$$L_i = -1400 + 24.5T_b \qquad (8)$$

be approximated from easily obtainable data.

Each of the three methods described gives values of similar magnitude. For common organic solvents the internal solvent pressures range from 1800 to 5000 atm[15] at 25°.

Conformations and Internal Pressure. Rotational barriers,[16] conformational populations,[17] and derived intermolecular and intramolecular interactions have historically been determined in the gas phase although similar determinations are now being made in the liquid phase using nuclear magnetic resonance. Nevertheless the fundamental quantities such as the rotational barrier of ethane and the populations of butane conformers are based on gas phase data. In the liquid phase these quantities are utilized in conformational discussions[18] although there should be substantial differences which would make these extrapolations imperfect. Since there is a range of internal pressures of liquids and these pressures exceed those of the gas phase by several thousand atmospheres it is reasonable to expect that the populations of various conformers of a substance should change from the gas phase to the liquid phase and within a variety of solvents of different internal pressures. This expectation is based on the fact that two conformations are unlikely to have the same molar volume. Thus with increasing solvent pressure the population of the conformer with the smaller molar volume should increase.

There is a sound basis for expecting different molar volumes of conformers as it is known that geometrical isomers exhibit density differences. Of importance to the development of the experimental work to be described in this paper is the observation that physical properties of the dimethylcyclohexanes are functions of molar volumes.[19] The dimethylcyclohexanes of diequatorial configuration are of lower density than the diastereomeric equatorial–axial compounds. Thus the densities of the compounds are in the order trans 1,2 < cis 1,2, cis 1,3 < trans 1,3 and trans 1,4 < cis 1,4. The boiling points, heat content, and refractive index are related to the density or molecular volume by the von Auwers–Skita rule.[20,21] In considering the differences in densities of the isomeric dimethylcyclohexanes it becomes obvious that an axial methyl group causes a diminution of molar volume as compared to an equatorial methyl group. An axial methyl

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(8) See ref 1, pp 289–314.
(9) See ref 2, pp 417–429.
(10) S. Glasstone, "Textbook of Physical Chemistry," 2nd ed, Van Nostrand, New York, N. Y., 1966, pp 479–480.
(11) W. J. Moore, "Physical Chemistry," 3rd ed, Prentice Hall, Englewood Cliffs, N. J., 1962, pp 712–713.
(12) J. H. Hildebrand and R. L. Scott, "Solubility of Nonelectrolytes," 3rd ed, Reinhold, New York, N. Y., 1950, Chapter V.
(13) See ref 12, pp 97–100.
(14) See ref 10, p 480.
(15) See ref 12, pp 435–439.
(16) J. P. Lowe, "Progress in Physical Organic Chemistry," Vol. 6, Interscience, New York, N. Y., 1968, pp 1–80.
(17) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, pp 5–35, 129–135.
(18) See ref 17, pp 5–35, 36–126.
(19) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 216.
(20) K. von Auwers, *Justus Liebigs Ann. Chem.*, **420**, 84 (1920).
(21) A. Skita, *Chem. Ber.*, **56**, 1014 (1923).

group is in a gauche conformation with respect to the C_1–C_2 ring carbon bond and the C_3-methylene group whereas an equatorial methyl group is in a trans conformation. These conformational differences and related density data provide support for the prediction that the trans conformation of butane is of higher molar volume than the gauche conformation. Such a prediction is also in accord with the differences in the densities of geometrical isomers of alkenes.

On the basis of the density data for dimethylcyclohexanes the expected differences in molar volumes for conformational changes about a single bond should be in the order of 2 cm^3 for substances of average molecular volume equal to approximately 100 cm^3. Thus for a change in internal pressure of 3000 atm the conformational equilibrium would be shifted by an energy increment of approximately 150 cal. While this quantity is small with respect to many other solvent effects the correction of gas phase data to liquid phase is potentially significant. The enthalpy difference between the trans and gauche conformations of butane is 800 cal.[22] When one considers the entropy of mixing for the two equivalent gauche conformers the free energy difference is less than the enthalpy difference by $RT \ln 2$. In the case of butane internal pressures of solvents can account for as much as 25% of the total free energy difference.

Theoretical Approaches

In order to establish the effect of internal solvent pressure on conformational populations there are distinct limitations which must be considered. Both the solvent and the solute should be nonpolar in order to avoid the possibility of polar interactions clouding the results. Dipole–dipole interactions are well-known contributors to conformational populations as evidenced by studies of α-halocyclohexanones[23] and dihaloalkanes.[24] Similarly, hydrogen bonding must be avoided as the energy of this interaction far exceeds that potentially due to internal solvent pressure, and it is well documented that conformational populations are strongly dependent on hydrogen bonding.[25]

Second, an equilibrium constant near unity between only two conformers is desirable. Only in such cases will the expected energy difference give rise to an easily detectable change in equilibrium constant. Finally, one has to consider the problem of determining the change in equilibrium constant. Nuclear magnetic resonance is ideally suited to evaluate the populations of rotamers on the basis of vicinal coupling constants.[26]

In terms of the nonpolar solvents to be used there are few limitations as the internal pressures of many liquids have been determined.[10,15] Therefore the compound to be examined is the limiting feature. Butane itself would fit the requirements of a nonpolar molecule and an equilibrium constant near unity. However, in order to detect conformational changes with internal solvent pressure, specifically deuterated compounds such as $CD_3CH_2CH_2CD_3$ would have to be examined and the vicinal coupling constant determined by ^{13}C satellite analysis. While such studies are planned, it was of concern to us to demonstrate first on experimentally more amenable molecules albeit of less fundamental and general importance that internal solvent pressure effects are indeed detectable.

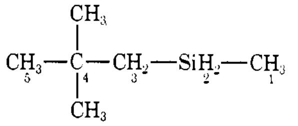
2-Silabutane derivatives were chosen for investigation because of their many advantages. Since the chemical shifts of Si–H containing compounds are in the vicinity of τ 6,[27] the resonance necessary to determine the $-SiH_2CH_2-$ vicinal coupling constant is well separated from other resonances. In addition since the coupling constant is in the order of 4 Hz,[27] the spectrum should be closely first order with $J/\Delta\delta \cong 0.01$ on a 100-MHz instrument.

In order to simplify further the spectrum of 2-silabutane and to provide a variety of nonpolar compounds it was desirable to prepare alkyl-substituted derivatives. However, at the same time these derivatives should not give rise to conformational equilibrium constants significantly diverging from unity. Since the rotational energy barrier for methylsilane is 1.7 kcal/mol[28] and the C–Si bond length is 1.8 Å,[29,30] substitution of alkyl groups on a 2-silabutane parent system should not cause as marked conformational changes as expected for alkanes.

Results and Discussion

The solvents chosen for this study are perfluoromethylcyclohexane,[30] carbon tetrachloride, benzene, and carbon disulfide with internal solvent pressures 1800, 3050, 3450, and 4250 atm, respectively.

The first substance examined was 4,4-dimethyl-2-silapentane (I) which has the experimental advantage that the C_3 methylene proton resonance is a simple triplet and can be observed at a position downfield from the C_1 methyl group but upfield from the *tert*-



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2-SiH_2-CH_3$$

I

butyl methyl protons. In Table I are listed the vicinal

Table I. Coupling Constants of Silicon Compounds

Solvent	$(CH_3)_3CCH_2SiH_2CH_3$ $J_{SiH_2CH_2}$	$(CH_3)_3CCH_2SiH_2CH_3$ $J_{SiH_2CH_3}$	$(CH_3)_2CHSiH(CH_3)_2$ J_{SiHCH}	$(CH_3)_2CHSiH(CH_3)_2$ J_{SiHCH_3}
C_7F_{14}	3.94	4.22	2.15	
CCl_4			1.99	
C_6H_6	3.84	4.21	1.92	3.84
CS_2	3.78	4.22	1.87	3.83

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(22) (a) K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940); (b) G. J. Szasz, N. Sheppard, and D. H. Rank, *ibid.*, **16**, 704 (1948); (c) R. A. Bonham and L. S. Bartell, *J. Amer. Chem. Soc.*, **81**, 3491 (1959).

(23) See ref 17, pp 460–469.

(24) K. K. Deb, *J. Phys. Chem.*, 71, 3095 (1957); F. Hruska, D. W. McBride, and T. Schaefer, *Can. J. Chem.*, **45**, 1081 (1967); R. J. Abraham, L. Cavalli, and K. G. R. Pachler, *Mol. Phys.*, **11**, 471 (1966); D. H. Williams and N. S. Bhacca, *J. Amer. Chem. Soc.*, **88**, 1155 (1966); H. Finegold, *J. Chem. Phys.*, **41**, 1808 (1964); J. Reisse, J. C. Celotti, and R. Ottinger, *Tetrahedron Lett.*, 2167 (1966); R. J. Abraham, L. Cavelli, and K. G. R. Pacher, *Nucl. Magn. Resonance Chem., Proc.*, 111 (1965); R. U. Lemieux and J. W. Lown, *Can. J. Chem.*, **42**, 893 (1964); F. A. L. Anet, *J. Amer. Chem. Soc.*, **84**, 747 (1962).

(25) M. Tichy, "Advances in Organic Chemistry," Interscience, Vol. 5, New York, N. Y., 1965, pp 115–298.

(26) P. Lazlo, "Progress in N.m.r. Spectroscopy," Pergamon Press, Vol. 3, New York, N. Y., 1967, Chapter 6, pp 245–258.

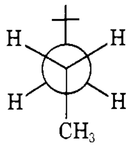
(27) E. A. V. Ebsworth and S. G. Frankiss, *Trans. Faraday Soc.*, **63**, 1574 (1967).

(28) D. Kivelson, *J. Chem. Phys.*, **22**, 1733 (1954); J. E. Griffiths, *ibid.*, **38**, 2879 (1963); R. W. Kilb and L. Pierce, *ibid.*, **27**, 108 (1957).

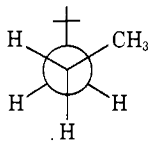
(29) K. W. Kilb and L. Pierce, *ibid.*, 27, 108 (1957).

(30) R. D. Dunlop, *J. Phys. Chem.*, **66**, 631 (1962).

coupling constants accurate to ±0.01 Hz for $-SiH_2CH_2-$ and $-SiH_2CH_3$. The spectra were run at 34° at concentrations of 5–7 vol % on a Varian Associates HA-100 operating in the HA mode. The reference lock employed was benzene or chloroform contained in a coaxial spacing capillary in order to avoid solvent pressure pertubations. In contrast to the $-SiH_2CH_3$ coupling constant which is insensitive to solvent, the $-SiH_2CH_2-$ coupling constant decreases with increasing solvent pressure. There are two nonequivalent conformations of 4,4-dimethyl-2-silabutane with Ib being favored by a statistical factor of 2 over Ia. In the Newman projections Ia and Ib the silicon atom is viewed at the front while the C_3 methylene is at the back. The time average coupling constant for Ia is $(J_{60} + J_{180})/2$ while that of Ib is $(3J_{60} + J_{180})/4$. Thus the observed coupling constant for SiH_2CH_2 is given by eq 9. In order to



Ia



Ib

$$J_{obsd} = N_{Ia}(J_{60} + J_{180})/2 + N_{Ib}(3J_{60} + J_{180})/4 \quad (9)$$

account for the decrease in the observed coupling constant with increased solvent pressure the population of Ib must increase at the expense of Ia. Such a conformational change is in accord with expectations of a smaller molecular volume for a gauche conformer as compared to a trans conformer.

In order to calculate the conformational equilibrium constant and determine the energy differences attributable to internal solvent pressure a means of evaluation J_{60} and J_{180} is necessary. Clearly the coupling constant for $-SiH_2CH_3$ is equal to $(2J_{60} + J_{180})/3$ but one equation is lacking to solve for the two unknowns. However the Karplus equation is known to be quite general with only the empirical parameters A, B, and C to be inserted.[31] The A term is equal to $(2J_{60} + J_{180})/3$ and C usually exceeds A by a small amount. B is usually small and of opposite sign than A and C. Therefore, an approximation of A, B, and C gives rise to an eq 11 which should yield reasonable values of J_{60} and J_{180}. The above relationship is applicable

$$J = A + B\cos\theta + C\cos 2\theta \quad (10)$$

$$J = 4.21 - 0.53\cos\theta + 4.74\cos 2\theta \quad (11)$$

only if there are no substituents introduced at the silicon or carbon atoms of the general formula $RSiH_2CH_3$. It is known that electronegative substituents cause a decrease in coupling constants and it has been suggested that the Karplus equation be multiplied by $(1 - a\Delta X)$ where a is a chosen proportionality constant and ΔX is the difference between the electronegativity of the substituent and hydrogen.[31] The magnitude of $a\Delta X$ for an alkyl group is 0.1 as evidenced by the change in coupling constant of 8.0 for ethane,[32,33] to 7.26 for propane.[34] Equation 11 represents parameters chosen from a compound containing one alkyl group. Therefore a more general form for H–C–Si–H systems is given by eq 12, where b is a proportionality constant chosen to represent the effect of an alkyl group and n is the number of alkyl groups. The value of b is chosen to be 0.09 based on the observed change in the coupling constant for SiH_2CH_3 in 4,4-dimethyl-3-silapentane and the $SiHCH_3$ coupling constant for 2,3-dimethyl-2-silabutane (Table I) in which there are one and two alkyl groups, respectively. Accordingly J_{60} and J_{180} for the $-CH_2SiH_2-$ fragment of 4,4-dimethyl-2-silapentane are 1.39 and 8.41, respectively. By using these values with eq 9 the equilibrium constants given in Table II are derived.

$$J = (4.68 - 0.60\cos + 5.28\cos 2\theta)(1 - bn) \quad (12)$$

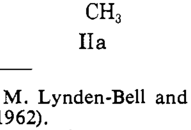
Table II. Conformation Equilibrium Constants

Solvent	Ia ⇄ Ib	IIa ⇄ IIb
C_7F_{14}	1.20	4.18
CCl_4		5.10
C_6H_6	1.51	5.62
CS_2	1.75	6.10

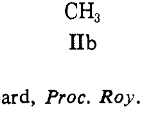
The population of Ia is less than that of Ib, but in terms of enthalpy Ia is probably favored since there is an entropy of mixing term favoring Ib. A plot of ln K *vs.* P_i yields a good correlation line, $r = 0.997$, shown in Figure 1 whose slope is equal to $-\Delta V/RT$ where $\Delta V = V_{Ib} - V_{Ia}$. The difference of molar volumes is -3.7 cm³/mol with the average molar volume estimated at 160 cm³/mol using an estimated density[35,36] of 0.7 g/ml. The ΔV corresponds to a 2% change which is entirely consistent with expectations.

Extrapolation of the line in Figure 1 to 1 atm gives $K = 1$ for the Ia ⇄ Ib equilibrium which corresponds to $\Delta H = 0.3$ kcal/mol after accounting for entropy of mixing. While the carbon–silicon bond is significantly longer than the carbon–carbon bond this small energy difference between trans and gauche conformations involving a methyl and *tert*-butyl group is remarkably small.

The coupling constants for 2,3-dimethyl-2-silabutane are given in Table I. Those for HSiCH were determined by irradiation at the $(CH_3)_2Si$ resonance using a Hewlett Packard 200-CD wide-band frequency oscillator and observing the Si–H resonance. In 2,3-dimethyl-2-silabutane (II) there are two nonequivalent conformations IIa and IIb. Again the silicon atom is viewed from the front in the Newman projection.



IIa



IIb

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[31] A. A. Bothner-By, "Advances in Magnetic Resonance," Vol. 1, Academic Press, New York, N. Y., 1965, pp 201–207.

[32] D. M. Graham and C. E. Holloway, *Can. J. Chem.*, **41**, 2114 (1963).

[33] R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **269**, 385 (1962).

[34] D. R. Whitman, L. Onsager, M. Saunders, and H. E. Dubb, *J. Chem. Phys.*, **32**, 67 (1960).

[35] The density of ethylisobutylsilane, dipropylsilane, and diisopropylsilane are 0.7166, 0.7183, and 0.7085 g/ml.[36]

[36] V. Bazant, U. Chvalousky, and J. Rathousky, "Organosilicon Compounds," Vol. 3, Academic Press, New York, N. Y., 1965, p 187.

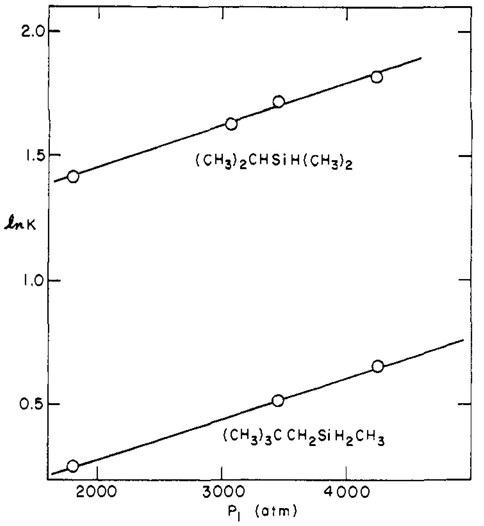

Figure 1. Correlations of conformational equilibria with internal pressure.

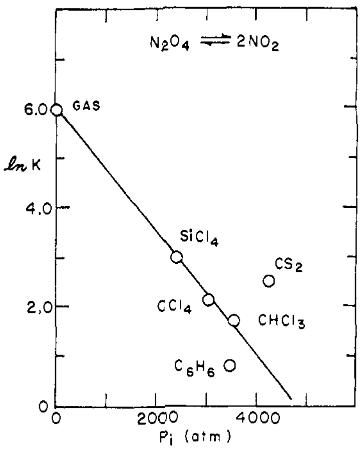

Figure 2. Effect of internal pressure on the dissociation of N_2O_4.

The J values for IIa and IIb are equal to J_{180} and J_{60}, respectively, and should give rise to a larger difference in the observed J than for 4,4-dimethyl-2-silabutane in which the change is muted by J_{60} contributions. Thus the observed coupling constant is given by eq 13. In order to evaluate J_{180} and J_{60} it is necessary to use $n = 4$ in eq 12. While the system was chosen to

$$J_{\text{obsd}} = N_{\text{IIa}}J_{180} + N_{\text{IIb}}J_{60} \tag{13}$$

yield a more substantial difference in J_{obsd} due to contributions of J_{60} and J_{180} the leveling effect of the alkyl groups conteracts this. As indicated in Table I the H–C–SiH coupling decreases with increasing solvent pressure while the coupling of $-HSi(CH_3)_2$ remains constant.

The equilibrium constants as a function of solvent are given in Table II. A plot of ln K *vs.* P yields the correlation line, $r = 0.985$, shown in Figure 1. The ΔV is -4.1 cm^3/mol for IIa $\rightleftharpoons$ IIb, a value again in accord with expectations for a substance with an average molar volume of 150 cm^3/mol.

Extrapolation of the line in Figure 1 to 1 atm gives $K = 3.1$ for the IIa $\rightleftharpoons$ IIb equilibrium which corresponds to $\Delta H = -0.4$ kcal/mol after accounting for entropy of mixing. While the predominance of IIb over IIa may be regarded as unexpected, it is not without precedent.[37] It is entirely possible that the bond distances involved in the silicon compounds move the energy of the H–H van der Waals interactions into a more favorable attractive portion of potential energy curve. This possibility will have to be examined closely for to date there is no other conformational data on organosilicon compounds.

Potential Uses of P_i. It is possible that internal solvent pressure may affect the rates of reactions and the position of equilibria. However, the energy difference should be small in most common solvents and the change in an equilibrium constant or a rate constant generally should not exceed an order of magnitude.

A review of selected data of reactions which should have a substantial volume of activation but which are insensitive to the polarity of the medium and do not experience specific solvation could reveal a valuable mechanistic criterion. At the present time the lack of pronounced solvent effects on reaction rates or equilibria is only qualitatively diagnostic.

Internal solvent pressure studies which are experimentally simpler than those of external pressure studies[38,39] may provide a rapid way to evaluate volumes of activation. Volumes of activation for Diels–Alder reactions as determined by external pressure are -20 cm^3/mol. Such a volume change will give rise to a rate change of 10 over a solvent pressure range of 3000 atm. Solvent effects in the range of a factor of 3–8 are observed.[40]

In the decomposition of acetyl peroxide the rate constant for the gas phase reaction at 85° exceeds the average rate of decomposition in common organic solvents,[41,42] by a factor of 1.6. Using an average internal solvent pressure of 3000 atm the volume of activation may be estimated as $+4.7$ cm^3/mol. Use of external pressure to determine the volume of activation of *tert*-butyl peroxide in toluene yields a value of $+5.4$ cm^3/mol.[38] Clearly the observed slowing of the rate of decomposition of acetyl peroxide in the liquid phase is commensurate with acceptable values of the volume of activation.

An example of the effect of internal pressure on an equilibrium is provided by the dissociation of N_2O_4 which has been studied in the gas phase and in a variety of solvents.[43] Internal solvent pressure accounts for the decrease in the equilibrium constant for dissociation as depicted in Figure 2. For the data in the gas phase, $SiCl_4$, CCl_4, and $CHCl_3$, the correlation coefficient is 0.998 and $\Delta V = +29$ cm^3/mol. A value of 20 cm^3/mol has been suggested.[44,45] The equilibrium constant in CS_2 is suggestive of a stabilization factor

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(37) See ref 17, pp 15–17.

(38) W. J. LeNoble, *J. Chem. Educ.*, **44**, 729 (1967).

(39) W. J. LeNoble, "Progress in Physical Organic Chemistry," Interscience, Vol. 5, New York, N. Y., 1967, pp 207–330.

(40) S. Patai, "The Chemistry of Alkenes," Interscience, New York, N. Y., 1964, p 918.

(41) M. Levy, M. Steinberg, and M. Szwarc, *J. Amer. Chem. Soc.*, **76**, 5978 (1954).

(42) F. G. Edwards and F. R. Mayo, *ibid.*, **72**, 1265 (1950).

(43) E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," 2nd ed, Oxford University Press, Oxford, England, 1947, p 184.

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for the NO_2 radical which may indicate association with the π bonds of the solvent. The equilibrium constant in benzene deviates from the correlation line in the opposite sense. This deviation may be indicative of a differential complexation effect with the N_2O_4 forming a better π complex than NO_2.

Oxidation by Palladium(II). II.[1] Products of the Oxidation and Isomerization of Phenylcyclopropane by Palladium(II)[2]

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Contribution from the Department of Chemistry,
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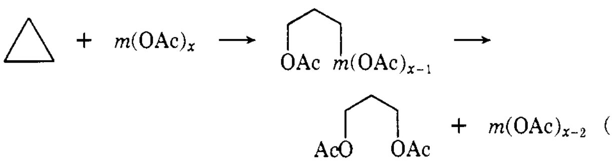
Abstract: The products of the oxidation of phenylcyclopropane by Na_2PdCl_4 in 2:1 glyme–water by volume are propiophenone and phenylacetone; the relative amount of each substance is controlled by the ratio of phenylcyclopropane to Na_2PdCl_4. At low ratios of phenylcyclopropane/Pd(II) a direct oxidation product, propiophenone, is favored whereas at high ratios an isomerization process to *trans*-propenylbenzene occurs which is followed by oxidation to phenylacetone. Oxidation to propiophenone in glyme–D_2O occurs without deuterium incorporation. Oxidation of phenylcyclopropane-*1-d* in glyme-water yields propiophenone-*2-d*, a product consistent only with consecutive hydride and deuteride shifts in a proposed 1,3-oxypalladium intermediate. Exchange of palladium for mercury in an 1,3-oxymercury adduct of phenylcyclopropane rapidly results in the formation of propiophenone.

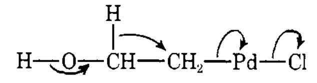
To date most studies of cyclopropane cleavage by heavy metal salts have involved species Hg(II),[4,5] Tl(III),[6] and Pb(IV)[7] which have filled d subshells. The mechanism of the oxidative cleavages by such metals are regarded as qualitatively similar. For the general reagent $m(OAc)_x$ the cleavage reaction proceeds as given in eq 1. It was of interest, therefore, to investigate the corresponding reaction with transition metals where vacant d orbitals and the attendant variety of coordination numbers and geometries might lead to interesting new reactions. The reactions of Hg(II), Tl(III), and Pb(IV) with olefins have been known for many years;[8] moreover, it was the well-documented similarity in the behavior of cyclopropanes and olefins toward electrophiles which prompted studies of cyclopropane oxidations by these metals originally.[9] It seemed plausible that in looking for a suitable transition metal to again consider the analogous olefin reactions.



(1)

Palladium chloride reacts with olefins to give carbonyl products.[10] The oxidation of ethylene to acetaldehyde by platinum group metals was known as early as 1894.[11] Today the reaction is the basis for the commercial production of acetaldehyde, the so-called Wacker process.[12]

The mechanism of palladium(II) oxidation of ethylene has been established on the basis of both product and kinetic studies.[13] A coordination complex in which both ethylene and hydroxide are bound to palladium is formed by a series of equilibrium steps. In the rate-determining step collapse of the coordination complex to a σ-bonded intermediate (1) occurs. A fast subsequent step involves reduction of palladium to its metallic state as it serves as a leaving group. The occurrence of a concomitant 1,2 hydride shift is supported by the facts that ethylene in D_2O yields acetaldehyde and ethylene-d_4 in H_2O yields acetaldehyde-d_4.[10]



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The similarity of the chemistry of cyclopropanes and olefins in their reactions with Hg(II), Tl(III), and Pb-

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[1] R. J. Ouellette and C. Levin [*J. Amer. Chem. Soc.*, **90**, 6889 (1968)] should be considered as the first report in this series.

[2] The authors acknowledge Grant 4765-ACl from the Petroleum Research Fund of the American Chemical Society in support of this research.

[3] Sinclair Oil Fellow 1967–1968.

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