ride and carbon monoxide (-226.0[31] and -26.4 kcal/mol,[30] respectively), the nature of the manganese-to-carbon and the manganese-to-phosphorus bonds must be similar. A similar relationship has been observed previously for a variety of cobalt carbonyl derivatives[2a,34] and in the data reported by Kiser, *et al.*,[26] for the carbonyl derivatives of nickel. It is also pointed out that the data for the heats of formation of the $(CH_3)_3SiMn(CO)_x^+$ ions are internally consistent for the values obtained from $(CH_3)_3SiMn(CO)_5$ and $(CH_3)_3SiMn(CO)_4PF_3$.

Using the relationship noted above (*i.e.*, substitution of PF_3 for CO lowers the ΔH_f° of the ion and the compound by 200 kcal/mol), it is possible to predict the values for the heats of formation of the remaining compounds in this series for which meaningful energetic measurements could not be obtained. These predicted values are as follows (kcal/mol): $\Delta H_f^\circ((CH_3)_3SiMn(CO)_3(PF_3)_2) = -823$, $\Delta H_f^\circ((CH_3)_3SiMn(CO)_2(PF_3)_3) = -1023$, $\Delta H_f^\circ((CH_3)_3SiMn(CO)(PF_3)_4) = -1223$.

Previous results[9,18,19] have shown that the average ionic bond energies are equal to the average neutral bond energies within 0.3 eV. Assuming this holds for the compounds reported here, the neutral hydrogen-manganese bond energy may be estimated using the technique described by Junk, *et al.*[9] This calculation for the H-Mn bond energy gives a value of 0.3 ± 0.5 eV (7 ± 12 kcal/mol), which supports previous claims[35,36] that this bond energy is very low.

Registry No. $HMn(CO)_5$, 16972-33-1; $(CH_3)_3SiMn(CO)_5$, 26500-16-3; $(CH_3)_3SiMn(CO)_4(PF_3)$, 33989-27-4; $(CH_3)_3SiMn(CO)_3(PF_3)_2$, 36087-62-4; $(CH_3)_3SiMn(CO)_2(PF_3)_3$, 36087-61-3; $(CH_3)_3SiMn(CO)(PF_3)_4$, 36087-60-2.

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Nuclear Magnetic Resonance Studies of Silicon-Nitrogen Compounds

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Received April 28, 1972

Variable-temperature proton magnetic resonance spectra were studied for a number of compounds containing silicon-nitrogen bonds in which potentially diastereotopic methyl groups were attached to nitrogen. Even at very low temperatures the methyl groups remained equivalent. It is concluded that rotational barriers about silicon-nitrogen bonds are lower than those about phosphorus- or sulfur-nitrogen bonds in analogous systems.

Introduction

There have recently been extensive studies by dynamic nuclear magnetic resonance spectroscopy of stereochemical phenomena in compounds containing sulfur-nitrogen[1,2] and phosphorus-nitrogen[3-5] bonds, which have been successfully interpreted in terms of a substantial rotational barrier about these bonds. We decided to extend these studies to the adjacent element in the third row of the periodic table, namely, silicon, and to look for rotational barriers about silicon-nitrogen bonds by dynamic proton magnetic resonance studies.

To this end we synthesized a number of compounds containing silicon attached to a dimethylamino group, including several chiral compounds. In these compounds if either inversion at nitrogen or rotation about the silicon-nitrogen bond were sufficiently slowed, the methyl groups attached to nitrogen would become diastereotopic and would, in principle at least, give rise to distinct magnetic resonance signals.

Experimental Section

Proton magnetic resonance spectra were determined on Varian A-60 and HA-100 spectrometers equipped with variable-temperature probes. The compounds used in this study were prepared by published methods,[6,7] and their physical and spectral properties agreed with published values.

Results

The results are presented in Tables I and II.

Discussion

As the results indicate, even at temperatures as low as −130°, there was no indication of the presence of diastereotopic methyl groups on nitrogen in the dimethylamino compounds or diastereotopic protons on the methylene groups in the aziridine and *N*-ethyl compounds examined. The experimental equivalence of the groups observed can have a number of possible explanations. It might be that the methyl groups are, in fact, diastereotopic but that the chemical shift difference due to the adjacent asymmetric silicon center is so small that the peaks are not seen as separate (*i.e*, $\Delta\delta$ must be less than about 0.5 Hz). This seems implausible in view of the large number of compounds studied, the large chemical shift differences induced in analogous systems containing chiral phosphorus[3-5] or sulfur[1,2] centers, and the

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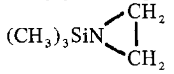
Table I. ^{1}H Nmr Parameters of $RR'R''SiN(CH_3)_2$

R	R′	R″	Solvent[a]	δ(R)[b]	δ(R′)[b]	$\delta(NCH_3)$[b]	T_L,[c] °C	$\Delta G_c^‡$(max),[d] kcal/mol
CH_3	CH_3	$N(CH_3)_2$	$CHClF_2$	0.0	0.0	2.45	−117	7.4
CH_3	$CH_2{=}CH$	$N(CH_3)_2$	$CHClF_2$	0.0	5.9	2.40	−120	7.3
CH_3	C_6H_5	$N(CH_3)_2$	CCl_3F	0.27	7.4	2.50	−130	6.8
CH_3	$CH_2{=}CH$	Cl	$CHClF_2$	0.18	6.2	2.18	−130	6.8
CH_3	CH_2Cl	Cl	$CHClF_2$	0.30	2.8 (δ_A) 3.2 (δ_B) (J_{AB} = 14.1 Hz)	2.30	−115	7.2
CH_3	C_6H_5	Cl	CCl_3F	0.90	7.5	2.6	−130	6.8

[a] Solutions were 10–15% v/v with 1% internal $(CH_3)_4Si$ as standard. [b] Chemical shifts are in ppm downfield from internal $(CH_3)_4Si$. [c] Lowest temperatures at which spectra were obtained. [d] See text.

Table II. ^{1}H Nmr Parameters of Other Silicon Compounds Studied ($CHClF_2$ Solvent)

	$\delta(CH_3Si)$[a]	$\delta(CH_2N)$[a]	$\delta(CH_3CH_2N)$[a]	T_L, °C	$\Delta G_c^‡$(max), kcal/mol
$(CH_3)_3SiN(CH_2CH_3)_2$[b]	−0.41	0.58	21.1	−100	8.3
	0.03	1.65		−120	7.3

[a] Chemical shifts are in ppm downfield from internal $(CH_3)_4Si$ as standard. [b] J_{HCCH} = 7.2 Hz.

fact that distinctly diastereotopic protons are evident in the chloromethyl group of the compound $ClCH_2Si(CH_3)(Cl)(N(CH_3)_2)$. In this compound, under the conditions reported in Table I, the protons of the chloromethyl group give rise to an AB quartet with J_{AB} = 14.1 Hz and with $\Delta\delta$ = 0.4 ppm (24 Hz at 60 MHz). This diastereotopic nature of these protons is clearly due to the adjacent chiral silicon center. In the analogous phosphorus compound, $ClCH_2P(Cl)(N(CH_3)_2)$, the protons of the chloromethyl group are also diastereotopic with J_{AB} = 12.8 and with $\Delta\delta$ = 0.27 ppm (16 Hz at 60 MHz).[8] In this phosphorus compound the methyl groups on nitrogen become diastereotopic at low temperatures with a chemical shift difference of 0.26 ppm at −80°. It seems reasonable to argue, by analogy, that in the silicon compound where an asymmetric silicon center is shown to lead to easily detectable diastereotopic methylene protons, slow rotation about the silicon-nitrogen bond or slow inversion at nitrogen would lead to *detectably* diastereotopic methyl groups on nitrogen.

The observation of diastereotopic methylene protons in the chloromethyl group of $ClCH_2Si(CH_3)(Cl)(N(CH_3)_2)$ also rules out the possibility that the failure to observe diastereotopic methyl groups on nitrogen at low temperature is due to a rapid exchange reaction occurring at silicon with concurrent inversion at silicon. Such a reaction would exchange the magnetic environments of both the methyl groups on nitrogen and the methylene protons of the chloromethyl group. Exchange processes of this type have been detected in this compound at high temperatures in the presence of added chloride ion,[8] and this exchange phenomenon will be discussed in detail in a later publication.

The results for *N*-trimethylsilylaziridine indicate very directly that the barriers to both inversion at nitrogen and rotation about the silicon-nitrogen bond are relatively small in this compound. The barrier to inversion at nitrogen in the model compound *N*-silylaziridine has recently been calculated,[9] by a parametrized CNDO/2 method, as 4.9 kcal/mol and our experimental results support this calculation and indicate that the barriers to rotation and/or inversion in the analog with methyl groups on silicon are probably less than 8 kcal. In earlier studies of the closely related *N*-trimethylsilyl-2,2-dimethylaziridine and *N*-trimethoxysilylaziridine similar results were noted.[10]

Table III. Calculated Values of $\Delta G_c^‡$ as a Function of $\delta\nu$; $\Delta G_c^‡ = 4.57T_c[9.97 + \log (T_c/\delta\nu)]$

	$\delta\nu$, Hz			
	0.5	1	5	10
T_c, °K	$\Delta G_c^‡$, kcal/mol			
100	4.42	4.56	4.88	5.01
110	4.86	5.01	5.36	5.51
120	5.30	5.47	5.85	6.02
130	5.74	5.92	6.34	6.52
140	6.19	6.38	6.83	7.02
150	6.63	6.83	7.31	7.52
160	7.07	7.29	7.80	8.02
170	7.51	7.75	8.29	8.52
180	7.95	8.20	8.78	9.02
190	8.40	8.66	9.26	9.53

The upper boundaries cited for $\Delta G_c^‡$ max in Tables I and II were calculated from the usual general equation for exchange between noncoupled sites:[11] $\Delta G_c^‡ = 4.57T_c[9.97 + \log (T_c/\delta\nu)]$ which itself derives from the value of the rate constant at coalescence being used in the Eyring rate expression, with the numerical values suitably expressed; if T_c is in degrees Kelvin and $\delta\nu$ is in hertz, $\Delta G_c^‡$ is obtained in calories per mole. This equation was used with the assumptions that T_c was below the lowest temperature reached in each case and that $\Delta\delta$, the chemical shift difference between the diastereotopic groups, would have been 5 Hz if the low-temperature spectra could have been observed; this assumes a somewhat more modest chemical shift difference than those seen in analogous phosphorus compounds.[8,12] Larger assumed values of $\delta\nu$ lead to somewhat larger values of $\Delta G_c^‡$, though the equation is not very sensitive to the value of $\delta\nu$ (see Table III).

The observational equivalence of the methyl groups on nitrogen in the compounds studied requires that the barriers to both inversion at nitrogen and rotation about the silicon-nitrogen bond be below the $\Delta G_c^‡$ (max) value quoted in the tables. If either barrier were larger than this quantity, then the methyl groups would become diastereotopic. The de-

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tailed discussion of the reasons for this which was earlier given for three-coordinate phosphorus compounds[4] is completely transferable to the present four-coordinate silicon compounds, with the substitution of one of the groups attached to silicon for the phosphorus lone-pair electrons. Since the purpose of this paper is to discuss rotational barriers, it follows from the above that the observed $\Delta G_c^{\ddagger}(\mathrm{max})$ must be an upper limit for the rotational barrier about the silicon-nitrogen bond.

This work also suggests that rotational barriers about silicon-nitrogen bonds are substantially lower than those about analogous phosphorus-nitrogen and sulfur-nitrogen bonds. In a set of (very roughly) analogous compounds the following barriers are observed: $CCl_3SN(CH_2Ph)_2$, 15.0 kcal/mol;[1] $CClH_2P(Cl)N(CH_3)_2$, 11.3 kcal/mol;[8] $CClH_2Si(CH_3)(Cl)(N(CH_3)_2)$, <7.2 kcal/mol (present work).

Recent theoretical analyses of the origins of rotational barriers in compounds amenable to *ab initio* molecular orbital calculations have shown that net rotational barriers are the result of a fine balance between attractive and repulsive interactions involving adjacent electron pairs and polar bonds.[13] In analyses of the "gauche effect" in second-row compounds ("the tendency of species containing adjacent electron pairs and/or polar bonds to exist preferentially in that conformation which has the maximum number of gauche interactions between these electron pairs or polar bonds"[14]) it seems that polar bond-polar bond interactions are greater than polar bond-lone pair interactions which are, in turn, greater than lone pair-lone pair interactions.

The compounds being compared in this study contain a third-row atom, bonded to other groups by polar bonds. The third-row atom (Si, P, S) is linked to nitrogen, bearing a lone pair of electrons, and also linked to other groups by polar bonds. There are many different types, and strengths, of interactions in these molecules, and it is premature to attempt to make a detailed analysis of them in view of the limited data available. Two observations may be germane; the observed barrier increases as the electronegativity of the atom attached to nitrogen (and the number of lone pairs of electrons it formally carries) increases. However in the phosphorus system, at least, the barrier decreases sharply[5] in going from a phosphonamidous chloride, $RP(Cl)NR'_2$, to the corresponding fluoride, $RP(F)NR'_2$. We have previously argued that this effect is best interpreted in terms of a p_π-d_π multiple-bond contribution to the rotational barrier,[5] but it must be conceded that the present negative observations in the silicon-nitrogen system do not indicate any very substantial p-d interaction with a geometric preference in this system.

In view of the relatively primitive level of our understanding of the bonding of third-row elements, it may be best to summarize these observations on rotational barriers as a set of provocative data in search of a reasonable explanation.

Registry No. Table I $R = CH_3$, $R' = CH_3$, $R'' = N(CH_3)_2$, 3768-58-9; $R = CH_3$, $R' = CH_2{=}CH$, $R'' = N(CH_3)_2$, 13368-45-1; $R = CH_3$, $R' = C_6H_5$, $R'' = N(CH_3)_2$, 33567-83-8; $R = CH_3$, $R' = CH_2{=}CH$, $R'' = Cl$, 25374-07-6; $R = CH_3$, $R' = CH_2Cl$, $R'' = Cl$, 36245-72-4; $R = CH_3$, $R' = C_6H_5$, $R'' = Cl$, 36245-73-5. $(CH_3)_3SiN(CH_2CH_3)_2$, 996-50-9; $(CH_3)_3Si$-$\overline{N{-}CH_2{-}C}H_2$, 2116-90-7.

Acknowledgments. This work was supported by Public Health Service Grant No. CA-07182 from the National Cancer Institute and by a grant from the President's Fund, California Institute of Technology. F. Fong was a participant in a National Science Foundation Undergraduate Research Program.

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Raman Spectra of Molten Bismuth Trichloride and Antimony Trichloride and of Their Mixtures with Potassium Chloride or Aluminum Trichloride[1a]

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Received April 17, 1972

Raman spectra have been obtained for solid and molten $SbCl_3$, molten equimolar $SbCl_3$-$AlCl_3$, $SbCl_3$-KCl mixtures, pure $BiCl_3$, equimolar $BiCl_3$-$AlCl_3$, and $BiCl_3$-KCl mixtures. The major species present in these samples have been postulated and their structures discussed.

Introduction

The crystal structure of solid $SbCl_3$ has been studied by X-ray diffraction.[2] The results show that there are discrete $SbCl_3$ molecules in the crystal located at sites with C_s symmetry. Nuclear quadrupole resonance experiments[3] indicate that the molecule in the crystal has a lower symmetry than C_{3v} because of intermolecular forces. However, only the four Raman lines of a typical C_{3v} molecule were reported for crystalline $SbCl_3$ by Krishnamurti.[4] Raman data on molten $SbCl_3$ are reported in several papers,[4-6] but the results show considerable disagreement. We, therefore, reinvestigated the Raman spectrum of $SbCl_3$ in order to clarify the situation. As a result of conductance measurements[7]

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