REARRANGEMENTS OF SILYL ENOL ETHERS

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
JUDITH A. McCLARIN
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T J Pinnavaia
Major professor

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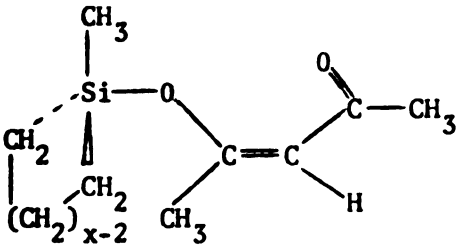
ABSTRACT

REARRANGEMENTS OF SILYL ENOL ETHERS

By

Judith A. McClarin

Silacycloalkane derivatives of acetylacetone, $CH_3Si(CH_2)_x(acac)$, (where x = 3, 4, and 5) have been prepared and characterized. The compounds possess an open chain enol ether structure which gives rise to configurations in which the uncoordinated oxygen is positioned cis (I) or trans (II) to the siloxy group.



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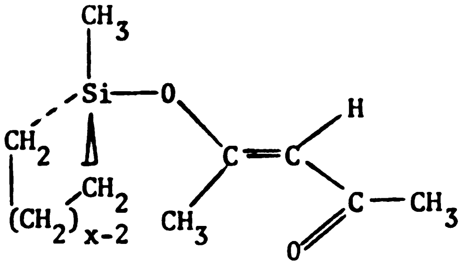

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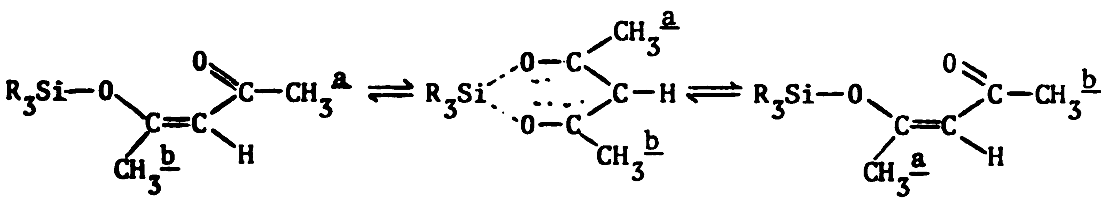
The cis isomer undergoes a rapid intramolecular stereochemical rearrangement which can be detected by nmr spectroscopy:



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The trans isomer is stereochemically rigid. Ring strain causes the cis to trans ratio to increase in the order $CH_3Si(CH_2)_5(acac) < CH_3Si(CH_2)_4(acac) < CH_3Si(CH_2)_3(acac)$, with values of 0.25, 0.45, and 2.23, respectively. The rate of the rearrangement increases in the same order with estimated relative rate constants at 25° of 2×10^3, 0.9×10^6 and 1×10^8 sec^{-1}, respectively.

Trimethylsilylhexafluroacetylacetone $(CH_3)_3Si(hfac)$ and trimethylsilyldipivaloylmethane $(CH_3)_3Si(dpm)$, where the substituent on the β-diketone is CF_3 and t-C_4H_9, respectively, were prepared and found to possess open chain enol ether structures. $(CH_3)_3Si(hfac)$ exhibits only the trans isomer and $(CH_3)_3Si(dpm)$ exhibits only the cis isomer. The large variation in the cis to trans ratio is explained by the differences in the long range electrostatic interaction between the silicon and the uncoordinated carbonyl oxygen. The rate of rearrangement at 25° for cis-$(CH_3)_3Si(dpm)$ is at least five orders of magnitude more facile than the analogous acetylacetone compound.

The chiral derivative cis-$(C_6H_5CH_2)(CH_3)(C_6H_5)Si(dpm)$ was prepared in order to follow the stereochemical course of the rearrangement by nmr spectroscopy. The difference in activation free energy for the low energy retention processes and a higher energy inversion processes is greater than 17.8 kcal/mole. The relative rate constants at 25° for the observed rearrangement processes and the inversion processes are estimated to be 1.1×10^6 and 1.5×10^{-7} sec^{-1}, respectively. More than 10^{13} rearrangements occur at 25° without inversion of configuration.

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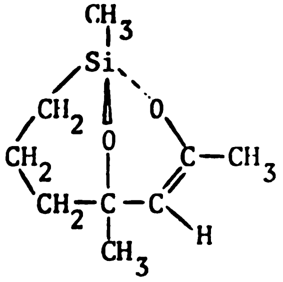
The above relationships between structure and lability show that the rearrangement involves the transformation of an incipient pentacoordinate ground state into a five coordinate intermediate by nucleophilic attack of the uncoordinated carbonyl oxygen on the silicon at an adjacent tetrahedral face or edge. The trigonal bipyramid intermediate has the β-diketonate spanning an axial-equatorial position. These displacement processes that occur with retention configuration at the triorganosilyl group can indeed involve the formation of a five-coordinate intermediate which may pseudorotate. Earlier views maintained that such processes are uncommon.

The methylsilacyclobutane derivative of acetylacetone $(CH_3)Si(CH_2)_3(acac)$ was observed to undergo an irreversible rearrangement involving opening of the silacyclobutane ring followed by a Michael-type addition to the acetylacetone moiety to give structure (III).



(III)

REARRANGEMENTS OF SILYL ENOL ETHERS

By

Judith A. McClarin

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1973

ACKNOWLEDGEMENTS

I would like to express my appreciation to Professor T. J. Pinnavaia. Through his guidance and patient efforts as a teacher I have acquired much. I wish to thank Professor C. H. Brubaker for being my second reader and for his interest during the past four years. I also wish to thank the Chemistry Department and Michigan State University for financial support and for the opportunity to acquire skills as a teacher.

I am deeply grateful to my parents, Mr. and Mrs. L. McClarin for their constant encouragement and love.

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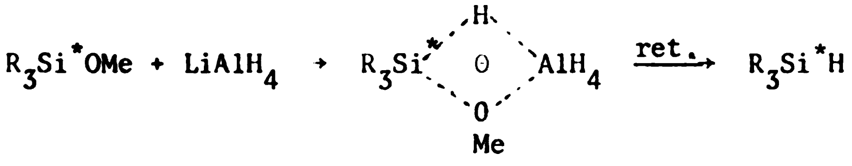
I. INTRODUCTION

Bimolecular nucleophilic displacement reactions at a triorganosilyl group may occur with retention or inversion of configuration. Several examples are summarized in Table I. Gielen[1] has recently interpreted the stereochemistry of these reactions in terms of the formation of five-coordinate R_3SiXY intermediates. Displacement reactions which occur with retention of configuration are believed to occur by the formation of a quasi-cyclic structure between the entering nucleophile and the leaving group. The reactions occur when the leaving group is a weak nucleophile (pK_a>10) and electrophilic assistance from the attacking species is necessary to separate the nucleophile from the silicon. Retention reactions are known for the displacement of hydride ions in a variety of solvents and alkoxy groups in non-polar solvents. A typical case involving retention of configuration is the reaction of R_3Si^*OMe and $LiAlH_4$ (Equation 1).

(1) 

$$R_3Si^*OMe + LiAlH_4 \rightarrow R_3\overset{*}{Si}\begin{array}{c} H \\ \ominus \\ O \\ Me \end{array}AlH_4 \xrightarrow{ret.} R_3Si^*H$$

In some cases, displacement of a fluoride ion occurs with retention, due to the coordinating ability of fluorine with electrophilic centers (Equation 2).

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Table I. Summary of Stereochemistry of Selected R_3Si^*X Displacement Reactions.

Reactant	Reagent	Product	Solvent	Stereochemistry
R_3Si^*H	$LiAlH_4$	R_3Si^*H	Bu_2O	retention
R_3Si^*H	KOH	R_3Si^*OH	xylene	retention
R_3Si^*H	$KO\text{-}t\text{-}C_4H_9$	$R_3Si^*O\text{-}t\text{-}C_4H_9$	$t\text{-}C_4H_9OH$	retention
R_3Si^*H	Cl_2	R_3Si^*Cl	CCl_4	retention
R_3Si^*H	$C_6H_5CO_3H$	R_3Si^*OH	CCl_4	retention
R_3Si^*OR	t-CuMgCl	R_3Si^*H	ether	retention
R_3Si^*OR	$LiAlH_4$	R_3Si^*H	ether	retention
R_3Si^*OR	KOH	R_3Si^*OK	xylene	retention
R_3Si^*F	R_3Si^*OK	$R_3Si^*OSiR_3$	xylene	retention
R_3Si^*F	EtLi	R_3Si^*Et	ether	retention
R_3Si^*OMe	MeOH	R_3Si^*OMe	MeOH	inversion
R_3Si^*OCOR	$LiAlH_4$	R_3Si^*H	ether	inversion
R_3Si^*OCOR	KOH	R_3Si^*OH	xylene	inversion
R_3Si^*OCOR	MeOH	R_3Si^*OMe	pentane	inversion
$R_3Si^*Cl(Br)$	H_2O	R_3Si^*OH	ether	inversion
$R_3Si^*Cl(Br)$	KOH	R_3Si^*OK	xylene	inversion
R_3Si^*Cl	ROH	R_3Si^*OR	pentane	inversion
$R_3Si^*Cl(Br)$	$NaBH(OMe)_3$	R_3Si^*OMe	ether	inversion
R_3Si^*Cl	CH_3CO_2K	R_3Si^*OCOMe	C_6H_6	inversion
$R_3Si^*Cl(Br)$	$LiAlH_4$	R_3Si^*H	ether	inversion
R_3Si^*F	$LiAlH_4$	R_3Si^*H	ether	inversion
R_3Si^*Cl	EtLi	R_3Si^*Et	ether	inversion

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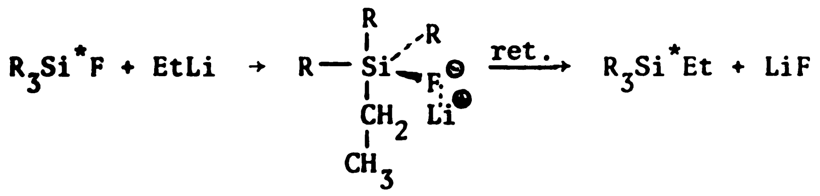
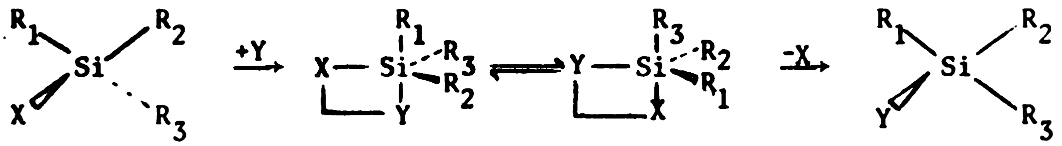
(2) 

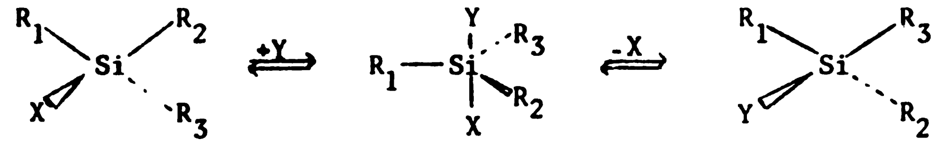
The strained, quasi-cyclic structure characteristic of retention reactions forces one of the electronegative groups in an equatorial position of the trigonal bipyramid. Pseudorotation would be rapid and the resulting stereochemistry would be retention (Equation 3).

(3) 

Inversion of configuration, during nucleophilic displacement, will occur when the leaving group is a good nucleophile, as in the displacement reactions of R_3Si^*OCOR (Equation 4).

$$(4) \qquad R_3Si^*OCOCH_3 + MeOH \xrightarrow{inv.} R_3Si^*OMe$$

The predominant result of halogen displacement is also inversion.[2] In general, inversion reactions may be described as going through a trigonal bipyramid intermediate where both electronegative groups may occupy axial positions (Equation 5).

(5)


Pseudorotation would be slow, since both electronegative groups are in electronically favorable positions.[4]

The solvent may effect the stereochemistry of the reaction in some cases. Methoxy exchange reactions in methanol occurs with inversion. In contrast, alkoxy displacements occur with retention in non-polar solvents.[2] Non-polar solvents favor intramolecular electrophilic assistance, whereas, polar solvents favor intermolecular assistance by solvent molecules.[1]

Gielen's views on the stereochemistry of nucleophilic displacement at a triorganosilyl group are related in part to the earlier mechanistic interpretations of Sommer. Sommer's classification of bimolecular displacement processes are summarized in Table II.

According to Gielen, nucleophilic displacement reactions involving R_3SiX compounds may be explained by one mechanistic approach where a stable five coordinate intermediate is formed which is sufficiently long lived to pseudorotate. The structure of this intermediate determines the stereochemistry of the reaction. Sommer believes that stable five coordinate intermediates are uncommon and that most of the nucleophilic reactions occur by concerted processes. He also believes that although the silicon 3d orbitals may, in certain cases, participate in the reaction, this does not mean that an intermediate is formed. The stereochemical data can be adequately explained by either approach. There is no evidence

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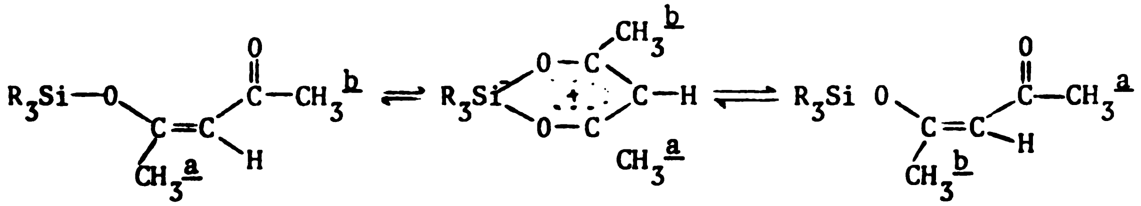
Table II. Sommer's Mechanisms[2] for Displacement Reactions at a Triorganosilyl Group.

Mechanism	Characteristics	Stereochemistry
S_N2 - Si	Common mechanism for polar reactions involving trigonal bipyramid transition state. Si may become electron rich compared to ground state. 3d orbital participation only if E_a is lowered: does not imply an intermediate.	Inversion for acyclic cases and retention for bridgehead Si
S_Ni - Si	Common mechanism involving frontside attack; may involve attack by strong nucleophiles. Formation of quasi-cyclic structure, no ion pair formation.	Retention
S_N2^* - Si	Rare mechanism involving formation of pentacoordinate intermediate in fast equilibrium step. Unable to distinguish kinetically from S_N2 - Si. [i.e. $R_3Si^*F + MeOH \rightarrow R_3SiF$]	Racemization
S_N2^{**} - Si	Rare mechanism involving formation of pentacoordinate intermediate in slow step, unable to distinguish kinetically from S_N2 - Si, no example.	No information

to support the existence of a five coordinate intermediate, nor is there any conclusive evidence to support the mechanisms proposed by Sommer.

The reversible intramolecular rearrangements of R_3SiX compounds, where one atom on X is displaced by another atom on the same ligand, represent systems in which structural and electronic parameters may be systematically varied without altering the basic displacement reaction. A typical rearrangement[5] is illustrated in equation 6 for a cis-triorganosilylacetylacetone, $R_3Si(acac)$.

(6) 

As illustrated by the data in Tables III and IV, the equilibrium cis to trans ratio as well as the rate of rearrangement, for the cis isomers of these compounds increases as the electron withdrawing ability of the silyl substituents increases, suggesting that a long range electrostatic interaction exists between the uncoordinated carbonyl oxygen and the silicon atom in the ground state of the cis isomer. The cis to trans ratios for $(C_6H_6)(CH_3)_2$ Si(acac)[6] and $(C_6H_5)_2CH_3Si(acac)$ are lower than expected based on Hammett-Taft σ^* values for C_6H_5 group and indicate a weakening of the long range interaction due to steric factors.[6]

Table III. Equilibrium Ratio of <u>Cis/Trans</u> Enol Ether Isomers for Triorganosilylacetylacetonates.[6]

Compound	[Cis]/[Trans]
$(n\text{-}C_4H_9)(CH_3)_2Si(acac)$	0.28
$(C_2H_5)(CH_3)_2Si(acac)$	0.29
$(CH_3)_3Si(acac)$	0.34
$(CF_3CH_2CH_2)(CH_3)_2Si(acac)$	0.39
$(CH_2 - CH)(CH_3)_2Si(acac)$	0.38
$(C_6H_5)(CH_3)_2Si(acac)$	0.31
$(C_6H_5)_2(CH_3)Si(acac)$	0.25

Table IV. Activation Energies for Intramolecular Rearrangements of Compounds Containing R_3Si Groups.

Compound	E_a Kcal/mole	Reference
R_3Si (acetylacetone)		6
R_3Si = $(n\text{-}C_4H_9)(CH_3)_2Si$	14.1	
$(C_2H_5)(CH_3)_2Si$	14.0	
$(CH_3)_3Si$	13.8	
$(CH_2{=}CH)(CH_3)_2Si$	13.0	
$(C_6H_5)(CH_3)_2Si$	<13.2>12.6	
$(CF_3CH_2CH_2)(CH_3)_2Si$	12.2	
$(C_6H_5)_2(CH_3)Si$	12.2	
$(CH_3)_3Si$ (triacetylmethane) (I)	15.4	7
$(2\text{-}C_4H_9)(CH_3)_2Si$ (tropolane) (III)	8.2[a]	9
$(CH_3)_3Si$ (pyrazole) (IV)		10
$R_3 = R_4 = R_5 = H$	$\sim$32	
$R_3 = R_5 = CH_3$, $R_4 = H$	28	
$R_3 = R_4 = R_5 = CH_3$	24	
$R_3 = R_5 = CF_3$, $R_4 = H$	<32	
R_3Si (1,3 dimethyltriazene) (V)		11
R_3Si = $(CH_3)_3Si$	16.1[b]	
$(CH_3)(C_2H_5)_2Si$	16.3	
$(CH_3O)_3Si$	14.8	
$(CH_3)(CH_3O)_2Si$	14.9	
$(CH_3)_2(CH_3O)Si$	15.1	
$(CH_3)(Cl)_2Si$	13.6	
$(CH_3)_2(Cl)Si$	13.8	

Table IV (cont'd)

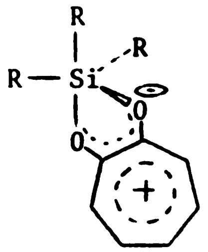
Compound	E_a Kcal/mole	Reference
$(CH_3)_3SiN(C_6H_5)COR$ (VIII)		14
R = $CHCl_2$	19.2	
CH_2Cl	17.5	
CH_3	11.2	
CH_2CH_3	11.6	
$CH(CH_3)_2$	9.5	
$(CH_3)_3Si$ (α-methylallyl)	47.7	22
$(CH_3)_2(C_6H_5)Si$ (α-methylallyl)	47.2	
$(CH_3)_2(C_6H_5)Si$ (α,β-dimethylallyl)	47.7	
$(CH_3)_3Si$ (α-phenylallyl)	42.5	

a. E_a determined by temperature dependence of C^{13} nmr

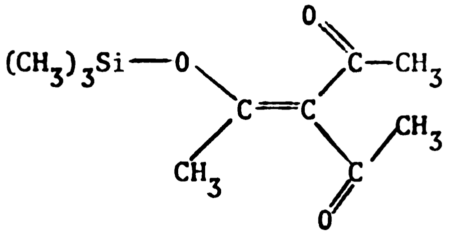
b. $\Delta G^{\ddagger}$ values

Analogous processes for R_3Si derivatives where the silyl group migrates between two oxygen atoms have been reported for triacetylmethane(**I**),[7] substituted malonate(**II**)[8] and tropolone(**III**)[9] derivatives. The rearrangements are facile, with activation energies of 15.4 kcal/mole for (I) and 8.2 kcal/mole for (III) and 13.8 kcal/mole for $(CH_3)_3Si(acac)$. The low activation energy of (III) supports the suggestion by Pinnavaia of a pentacoordinate intermediate for these reactions, since here the dipolar species is highly stabilized.[9]

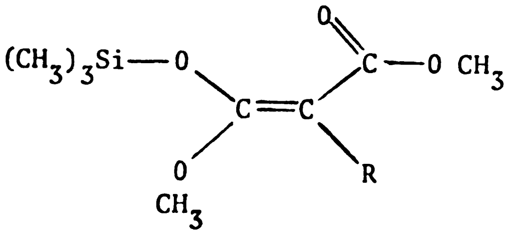
Substituent effects on the *cis/trans* ratio were observed for II.



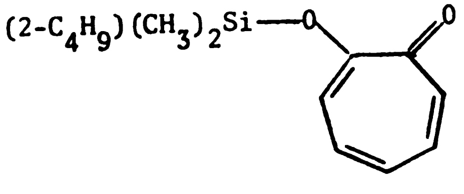
When R = H or Me, only the *cis* isomer is observed, but when R = Ph, 10% trans isomer is observed,[8] most likely due to steric effects.



I (Ref.7)

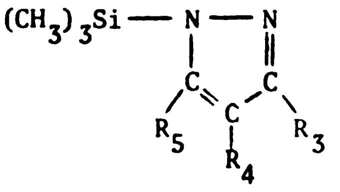


II (Ref.8)

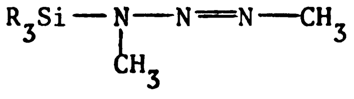


III (Ref.9)

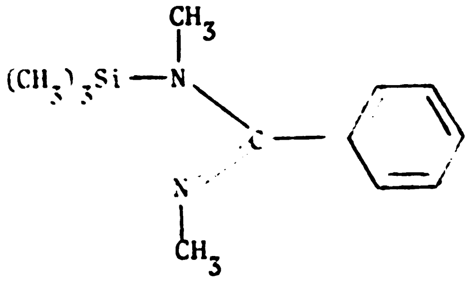
Rearrangements where the silyl group migrates between two nitrogens have been reported for R_3Si derivatives of pyrazole(IV),[10] triazine(V),[11] benzamidene(VI),[12] and for silyl hydrazine anions(VII).[13] Enhanced rearrangement rates for substituted pyrazoles are observed as the 3, 4, and 5 substituents become more electron releasing (cf., Table IV). The increase in electron density at the uncoordinated nitrogen would increase the extracoordinate silicon-nitrogen interaction. If the increase in electron density had the effect of strengthening the silicon-nitrogen bond the opposite effect would be observed. Steric repulsions between the 3, 5 substituents and the trimethylsilyl group would be relieved in a pentacoordinate activated complex leading to a decrease in activation energy when H is replaced by methyl in the 3,5 positions.[10] The activation energy of rearrangement for (V) is lowered as the silyl substituents become more electron withdrawing.[11] The magnitude of this substituent effect is comparable to that observed for $R_3Si(acac)$ (Table IV).



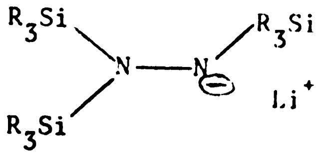
IV (Ref. 10)



V (Ref.11)

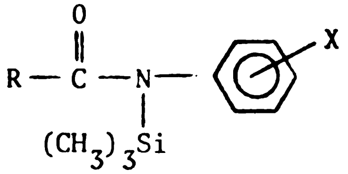


VI (Ref.12)

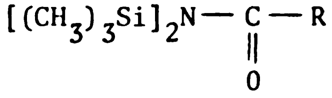


VII (Ref.13)

Migration between nitrogen and oxygen is observed in trimethylsilyl anilides(VIII) and amides(IX), as well as in the more complex disiloxadiazines(X). The activation energy for rearrangement of the anilides decreases as electron releasing substituents are placed on the carbonyl group[14] (cf., Table IV). This result is similar to the effect of substitution on the pyrazole ring. It has also been observed that the equilibrium concentration of O-silylated isomer increases with increasing electron withdrawing ability of the phenyl substituents.[17] An interaction between the uncoordinated oxygen and silicon referred to as incipient pentacoordination, exists in disiloxadiazines (X).[16,17] The interaction was established in the solid state by x-ray diffraction studies.[18] The distance between the exocyclic oxygen and silicon is 0.74 Å less than the sum of the Van der Waals radii, but still longer than a silicon-oxygen covalent bond. The geometry of the incipient pentacoordinate silicon is distorted toward a trigonal bipyramid.

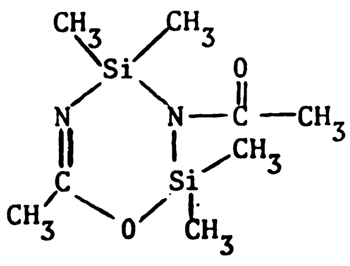


VIII (Ref.14,17)



$[(CH_3)_3Si]_2N-\underset{\underset{O}{\|}}{C}-R$

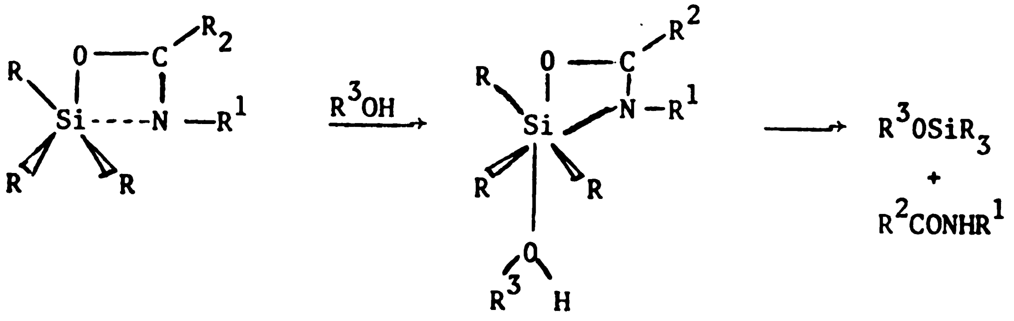
IX (Ref.15)



X (Ref.16,17)

The superior silylating ability of triorganosilylamides compared to triorganosilylamines can be explained by the incipient pentacoordinate geometry of the silylamides in the ground state.[17] The reaction with a proton donor may be described as the transformation of a trigonal bipyramid or tetragonal pyramid ground state to an octahedral transition state. (Equation 7)

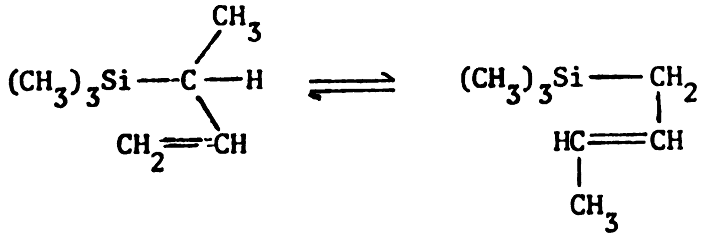
(7)



The lower activation energy for the reaction of silylamides compared to silylamines is due to the already expanded valence shell of silicon in the silylamide.

The fluxional character of trimethylsilyl groups is also found in the intramolecular rearrangement of trimethylsilylcyclopentadiene,[19,20] and the rearrangements of trimethylsilylindine[21] and allylic silanes.[22] In contrast to the rearrangements of R_3Si groups between electronegative atoms, the rearrangement of allylic silanes (Equation 8) is uneffected by substitution at the silicon. The only substituent influence on rate

(8)



occurs when one product is clearly stabilized by the substituent.[22] This effect is expected in a concerted rearrangement process.[23] The activation energy for this process is considerably greater than those observed for the degenerate processes (cf., Table IV).

Triorganosilyl β-diketonate and triorganosilyltropolone are known to rearrange with retention of configuration at silicon,[9,24] as do silyl carbinols and β-ketosilanes.[25,26] The presence of a cyclic structure in the activated complex, such as the one shown in Equation 6 for R_3Si acac, indicates a similarity to the retention case of bimolecular nucleophilic displacements.

As a general case, the facile rearrangement of R_3SiX——Y may be explained as an incipient pentacoordinate ground state transformed into a pentacoordinate intermediate.[1,6,9,17] Evidence available at present tends to support this mechanism. The suggestion has been made that triorganosilyl compounds may undergo pseudorotation, similar to the phosphoranes.[3,6] The purpose of this research is to elucidate further the kinetics and mechanism of the rearrangement of R_3Si β-diketonates. We have studied the effect of ring strain on the reactivity and measured the difference in activation free energy between the retention and inversion process.

II. EXPERIMENTAL

A. Reagents and Solvents

Methyl(3-chloropropyl)dichlorosilane was obtained from the Chemical Research Division of the Dow-Corning Corporation and was used without further purification. All other silicon reagents were obtained from Aldrich Chemical Company and were fractionally distilled in an N_2 atmosphere before use. The purity of reagents was checked by nmr spectroscopy.

Diethylether, benzene, hexane and tetrahydrofuran were dried for at least 24 hours over lithium aluminum hydride and freshly distilled before use. Methylene chloride, carbon tetrachloride and chlorobenzene were dried over calcium hydride for at least 24 hours and freshly distilled before use. α-Chloronapthalene was dried over molecular sieves, and carbon disulfide was dried over phosphorus pentaoxide.

Pyridine was distilled from and stored over Drierite. Magnesium turnings and powdered magnesium was degassed under vacuum overnight before use.

B. Syntheses

General Synthetic Techniques

All glassware was dried at 175°C overnight and cooled in a disiccator whenever possible. All manipulations of hydroscopic reagents and products were carried out in a nitrogen atmosphere. Liquid products were purified by fractional distillation through a 12-cm jacketed Vigreaux column.

Trimethylsilylhexafluroacetylacetone[27]

A solution of 11.7g (0.056 mol) of hexafluroacetylacetone and 20ml (0.157 mol) of trimethylchlorosilane was heated at reflux temperature for eleven days. The reaction mixture was distilled, at atmospheric pressure to give trimethylsilylhexafluroacetylacetone in 43% yield (b.p. 128-129°). Anal. Calculated for $C_8H_{10}F_6O_2Si$: C, 36.0; H, 3.57; F, 40.7; Si, 10.0. Found: C, 34.9; H, 4.01; F, 40.6; Si, 10.9.

Trimethylsilyldipivaloylmethane

The sodium salt of dipivaloylmethane 10.4g (0.05 mol) dissolved in 50ml ether was added slowly to a solution of 5.9g (0.054 mol) trimethylchlorosilane in 50ml ether. The reaction mixture was stirred for two hours, and the resulting sodium chloride was removed by filtration. Distillation of the mixture under reduced pressure gave a colorless liquid product (b.p. 44-45°; 0.04 torr). The yield was 51%. The sodium salt used in the reaction was prepared by the reaction of dipivaloylmethane and sodamide or sodium metal. Anal. Calculated for $C_{14}H_{28}O_2Si$: C, 65.6; H, 11.0; Si, 11.0. Found: C, 66.2; H, 11.2; Si, 11.6.

Benzylmethylphenylchlorosilane

Benzylmagnesium chloride was formed by the slow addition of 90ml (0.78 mol) benzylchloride to 19g (0.78 mol) magnesium turnings in 700ml ether. After the mixture had been allowed to reflux for one hour, it was cooled to -78° in a dry-ice acetone slush bath and 100ml (0.78 mol) methylphenyldichlorosilane and 1000ml ether were added rapidly. The reaction mixture was stirred and allowed to warm slowly to room temperature overnight. The solid was filtered from the slurry, and the ether was removed under reduced pressure. The remaining liquid was distilled under reduced pressure to give a colorless liquid product (b.p. 100-105°; 0.1 torr). The yield was 51%. The purity of the product was checked by integration of CH_3, $-CH_2$, and $-C_6H_5$ nmr lines.

Benzylmethylphenylsilyldipivaloylmethane

The preparation of this compound is analogous to the preparation of trimethylsilyldipivaloylmethane. Distillation of the product under reduced pressure gave a viscous pale yellow product (b.p. 183-185°; 0.1 torr). The yield was 51%. Anal. Calculated for $C_{25}H_{34}O_2Si$: C, 76.09; H, 8.68; Si, 7.12. Found: C, 76.34; H, 8.60; Si, 7.05.

Methylchlorosilacyclobutane[28]

Powdered magnesium 18.3g (0.75 mol) was activated by grinding with a mortar and pestle in a nitrogen atmosphere and then heating it for 15 minutes at reflux temperature in 200ml ether containing 2ml of 1,2-dibromoethane. The magnesium slurry was cooled to room temperature and 39.9ml (0.25 mol) methyl(3-chloropropyl)dichlorosilane, in 200ml ether was added slowly over several hours. The mixture was refluxed overnight, cooled to room temperature, and then stirred for 24 more hours. The product was separated from the filtrate by fractional distillation at atmospheric pressure (b.p., 101-102°; Lit.[28] 103.5-104°, 731 torr). The yield was 60%.

Methylchlorosilacyclopentane[29]

To a mixture of 22g (0.90 mol) magnesium in 500ml ether, was added slowly 50.8g (0.400 mol) 1,4-dichlorobutane. The mixture was stirred for 4-5 hours until the ether stopped refluxing. The resulting difunctional Grignard reagent was transferred to a large dropping funnel and added slowly to 38.5g (0.360 mol) methyltrichlorosilane in 1 liter of ether. The mixture was heated at reflux temperature for 4 hours and then stirred at room temperature overnight. The slurry was filtered and the ether removed by distillation at atmospheric pressure. The remaining mixture was filtered and distilled at atmospheric pressure to give a colorless liquid product (b.p. 128-129°; Lit.[29] 132). The yield was 31%.

Methylchlorosilacyclohexane[29]

The preparation of this compound is analogous to the preparation of methylchlorosilacyclopentane. Purification of the product by distillation, at atmospheric pressure gave a colorless liquid (b.p. 160-188°; Lit.[29] 167°). The yield was 34%.

Cyclic Organosilyl Acetylacetone Derivatives

The general method was modified from the preparation of trimethylsilylacetylacetone.[6] A solution of pyridine (*ca*., 0.1 mol) in hexane (*ca*., 20ml) was added slowly to equimolar amounts (*ca*. 0.1 mol) of acetylacetone and the silane in hexane (*ca*., 80ml). The mixture was allowed to stir at room temperature overnight, except in the reaction with the silacyclobutane, in which case the mixture was stirred for one hour. The pyridinium chloride was filtered, and the hexane was removed under vacuum. The remaining liquid residue was filtered again and distilled under reduced pressure. Boiling points, yields, and analytical data is presented in Table V.

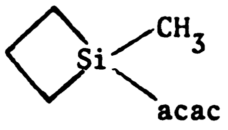
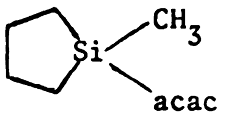
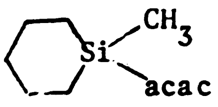
Rearrangement Product of Methyl(acetylacetonato)silacyclobutane

The silacyclobutane derivative was found to rearrange at room temperature, and was stored in dry-ice. The rate of rearrangement was dependent on the purity of the sample. A highly purified sample had undergone approximately 50% rearrangement in 2 weeks. The rearrangement product was purified by distillation at reduced pressure (b.p. 36-37°; 0.5 torr). Anal. Calculated for $C_9H_{16}O_2Si$; C, 58.65; H, 8.75; Si, 15.24; M.W., 184. Found: C, 58.66; H, 8.77; Si, 15.46; M.W., (in CCl_4) 193.

1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane[30]

A small portion of 284g (1.73 mol) chloromethyldimethylchlorosilane and a few drops of iodomethane to initiate the reaction was added to a mixture of powdered magnesium (ca., 2g) in tetrahydrofuran. The remaining silane and enough tetrahydrofuran to bring the volume to 500ml was then added. The remaining magnesium (70.2g, 2.89 mol) was added over a period of 2 1/2 hours. The temperature was kept between 30° and 50° during the addition, and then the mixture was heated to 50° for an additional 2 hours. The reaction mixture was washed successively with 500ml, 300ml, and 100ml water and then dried over magnesium sulfate. The product was purified by distillation under reduced pressure to give a colorless liquid (b.p. 108-112°; 50 torr, Lit.[31] 112°; 50 torr). The identity of the product was further verified by infrared spectroscopy. The yield was 14%.

Table V. Synthesis and Analytical Data for Cyclic Organosilyl Enol Ethers.

Compound	Boiling Point, °C	Yield,%	Calculated			Found		
			C	H	Si	C	H	Si
	54-55 (0.5 torr)	22	58.65	8.75	15.24	58.63	8.82	15.39
	78-80 (0.2 torr)	24	60.56	9.15	14.16	59.50	8.78	14.43
	67-68 (0.1 torr)	25	62.09	9.45	13.20	61.78	9.51	13.38

1,3,5,7-tetrasilaadamantanes[31]

A mixture of 10.4g (0.078 mol) aluminum chloride, and 17g (0.078 mol) 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane, was heated to 100° for 2 hours. The tetramethylsilane which was formed was continuously distilled from the reaction mixture. The reaction mixture was cooled, diluted with 200ml benzene and washed twice with 50ml water. The organic layer was dried over magnesium sulfate, and the benzene was removed under vacuum. White crystals were vacuum sublimed at room temperature from the resulting oil. The infrared spectrum showed a Si-Cl stretch at 527 cm^{-1}, and silver chloride was precipitated from a nitric acid solution of the product. The nmr spectrum of the product indicated a mixture of silaadamantanes which were identified as 1,3,5,7-tetramethyl-1,3,5,7-tetrasilaadamantane and 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane by comparison of chemical shift values to reported values[32](b.p. 114-127°).

C. Analytical Data

Microanalysis of compounds was performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

D. Infrared Spectra

Infrared spectra of silyl enol ethers were determined as 5% by volume solutions in carbon tetrachloride or methylene chloride by use of Perkin Elmer 237B and Perkin Elmer 457 spectrometers. Matched liquid cells with KBr salt windows and a 0.1mm path length were used for difference spectra of the solutions. The 2851 and 1603 cm^{-1} bands of polystyrene were used as reference frequencies.

E. Nuclear Magnetic Resonance Spectra

Proton magnetic resonance spectra were obtained by use of a Varian A56/60D analytical spectrometer operated at 60MHz. The probe temperature was controlled to ± 0.5° with a Varian Model V-6040 temperature control. Temperatures were determined to ± 0.5°, by use of a copper-constantan thermocouple inserted just below the sample tube and above the heat sensor. Magnetic sweep widths were calibrated by the audiofrequency side band technique. Tetramethylsilane was used as an internal standard, and chemical shift values were determined by positioning the side band of TMS over the resonance of interest. Integration of resonance lines was performed by planimetry.

All spectra were recorded at a radiofrequency field strength well below the value necessary to observe the onset of saturation.

F. Preparation of Solutions for IR and NMR Studies

All solutions used in the infrared studies were prepared in a nitrogen filled glove bag and transferred to liquid cells while in an N_2 atmosphere.

Sample tubes for the nmr studies were dried as described in section II B. When possible, solutions were prepared in a nitrogen filled glove bag, and the tubes were sealed with a flame. Solutions of silane and chlorodifluromethane were prepared by distilling the solvent to the nmr tube on the vacuum line.

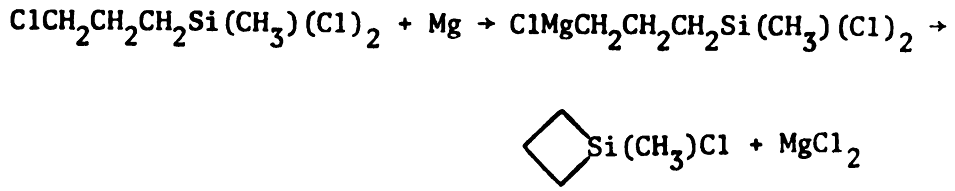
All solvents were dried as described in section II A. Samples were used immediately after preparation since decomposition due to hydrolysis occurred upon ageing, even in a sealed tube.

III. RESULTS AND DISCUSSION

A. Preparation and Characterization of Cyclic Organosilyl Acetylacetone Derivatives

The chlorosilanes used as starting materials in the preparation of the cyclicorganosilyl acetylacetone derivatives were synthesized by means of grignard reactions. Methylchlorosilacyclobutane was prepared by the ring closure reaction of methyl (3-chloropropyl)dichlorosilane with magnesium (Equation 9). Earlier work has shown that in

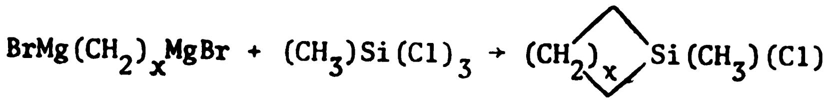
(9)



$$ClCH_2CH_2CH_2Si(CH_3)(Cl)_2 + Mg \rightarrow ClMgCH_2CH_2CH_2Si(CH_3)(Cl)_2 \rightarrow Si(CH_3)Cl + MgCl_2$$

order to obtain reproducibility good yields, increasing the surface area of the magnesium, as well as chemical activation is essential.[28,33] Methylchlorosilacyclopentane and methylchlorosilacyclohexane were both prepared by the reaction of the appropriate difunctional grignard reagent with methyltrichlorosilane (Equation 10). The presence of

(10)



$$BrMg(CH_2)_xMgBr + (CH_3)Si(Cl)_3 \rightarrow (CH_2)_x Si(CH_3)(Cl)$$

chlorine atoms on the silicon facilitates the ring formation.[29] The reaction proceeds in higher yields with silicon tetrachloride as a substrate, but subsequent replacement of a chlorine with a methyl grignard produced only small amounts of the desired product. In all three cases the ether solvent was removed by slow distillation through a vigreaux column. A substance co-distilled with the ether, if the distillation was not executed slowly. This substance hydrolyzed readily on contact with air to give an acidic gas.

The cyclic organosilyl acetylacetone derivatives were prepared by the reaction of the cyclic chlorosilane, acetylacetone, and pyridine (Equation 11). An analogous reaction was originally described by West[34]

(11) $CH_3Si(CH_2)_xCl + H(acac) + py \rightarrow CH_3Si(CH_2)_x(acac) + py \cdot HCl$

for the preparation of $(CH_3)_3Si(acac)$. To avoid ring-opening side reactions, the procedure was modified by keeping the reaction mixture at room temperature instead of heating it to reflux temperature.

The compounds were pale yellow liquids which hydrolyzed on contact with moist air. The silacyclohexane and dislacyclopentane derivatives, after ageing at room temperature for 2 months in a vial sealed under nitrogen and stored in a desiccator, showed only a small amount of decomposition, as judged by nmr spectroscopy. The silacyclobutane derivative was appreciably less stable even when highly purified. Inspection of the nmr spectrum after ageing at room temperature under the above conditions, indicated that more than one decomposition reaction occurs.

Silacyclobutanes are known to be much less thermally stable than the 5 and 6 member ring compounds and will undergo ring opening reactions to form polymers.[35] The decomposition products are high boiling and may be separated from the compound by distillation. In addition to a probable polymerization reaction, the silacyclobutane derivative undergoes a rearrangement reaction which is catalyzed by unknown impurities, but is observed to occur at a lower rate even in highly purified samples. Analysis of the rearrangement product, which was purified by fractional distillation, has shown it is a monomer with the same stoiciometry as $CH_3Si(CH_2)_3(acac)$. The ambient temperature nmr spectrum of the product in CCl_4 solution is shown in Figure 1 along with the spectrum of $CH_3Si(CH_2)_3(acac)$. The spectrum contains singlets at τ9.78 and τ8.79, a doublet centered at τ8.23 (τ=.95 Hz), a quartet centered at τ4.80 (τ=.95 Hz) and a complex series of lines between τ9.4 and τ8.2. There is no temperature dependence of the nmr spectrum between 120° and -80°C. In the infrared spectrum of the rearrangement product (Figure 2) there is a strong band at 1657 cm^{-1}, which is within the proper region for an isolated double bond, usually found between 1680-1620 cm^{-1}.[36] There is a weaker band at 1586 cm^{-1} which may be assigned to the coordinated alkoxide, usually found between 1500 cm^{-1} and 1600 cm^{-1}.[34] A Si-O frequency at 1050 cm^{-1} and a Si-C stretch at 840 cm^{-1} are also present. No change was observed in the nmr spectrum of the compound after it had aged for 2 months at room temperature.

A structure consistent with the above data is shown below. The nmr lines may be assigned as follows: the $Si-CH_3$ singlet at τ9.78,

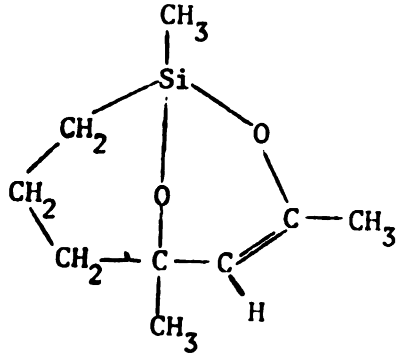


Figure 1. Proton nmr spectra (60 Mhz) of A) $CH_3Si(CH_2)_3(acac)$ in CCl_4 (25 ml/100 ml solvent), B) the thermal rearrangement product of $CH_3Si(CH_2)_3(acac)$ in CCl_4 (25 ml/100 ml solvent), and C) the methanolysis product of the rearranged form in CCl_4 (25 ml/100 ml solvent).

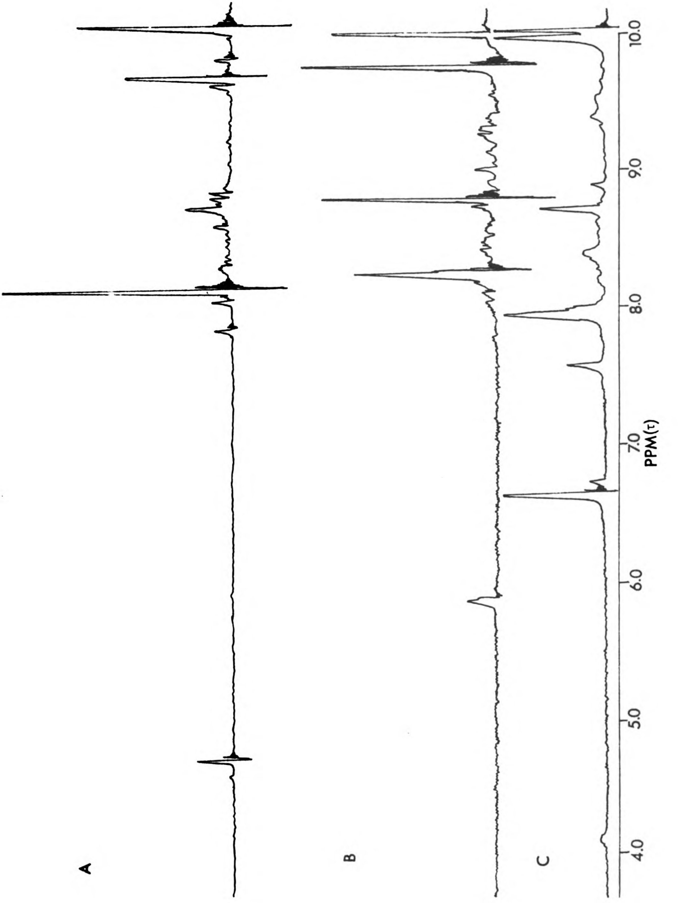
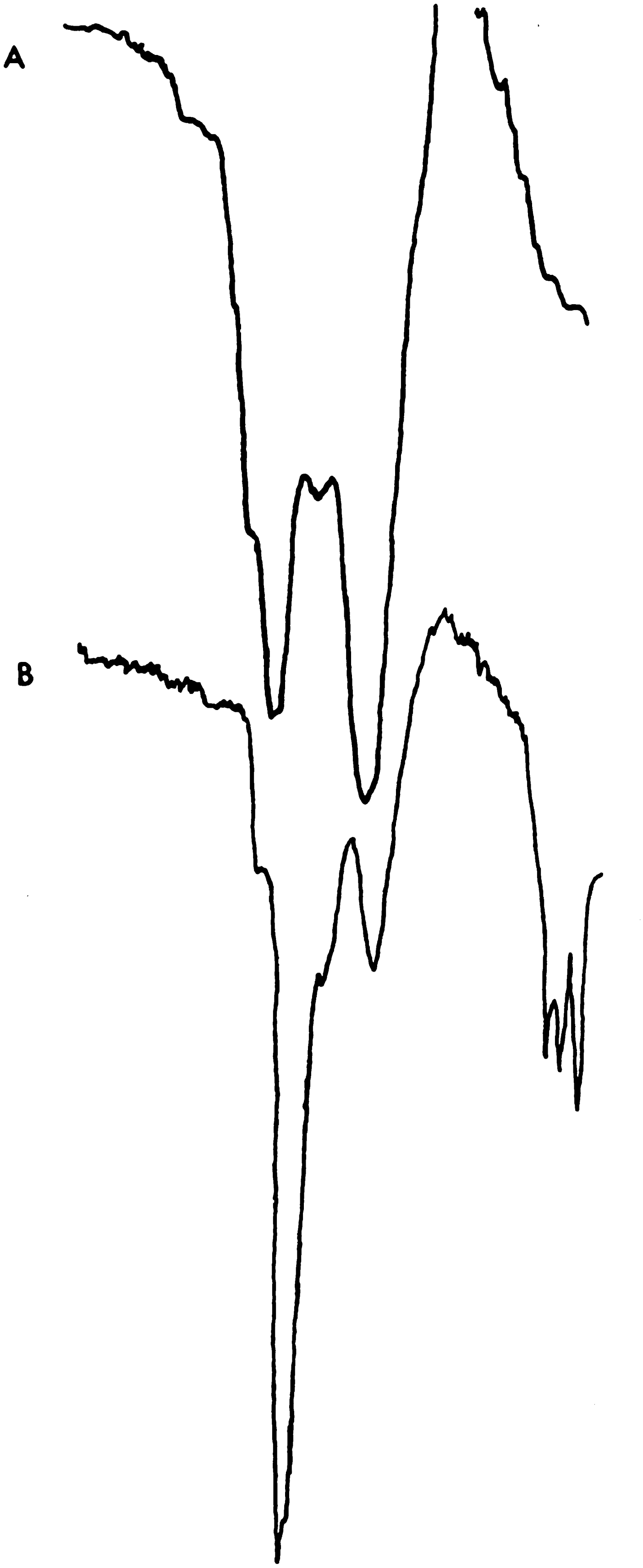
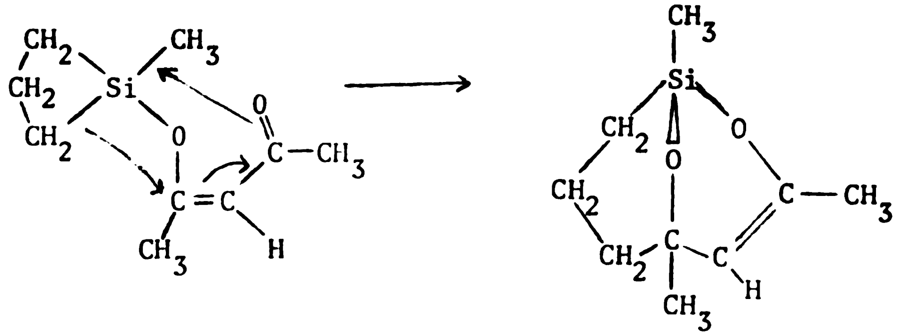

A
B
C
4.0
5.0
6.0
7.0
8.0
9.0
10.0
PPM(τ)

Figure 2. Infrared spectra of A) $CH_3Si(CH_2)_3(acac)$ in CH_2Cl_2, (5 ml/100 ml solvent), B) the thermal rearrangement product of $CH_3Si(CH_2)_3(acac)$ in CCl_4 (5 ml/100 ml solvent), in the region 1800 cm^{-1} to 1400 cm^{-1}.

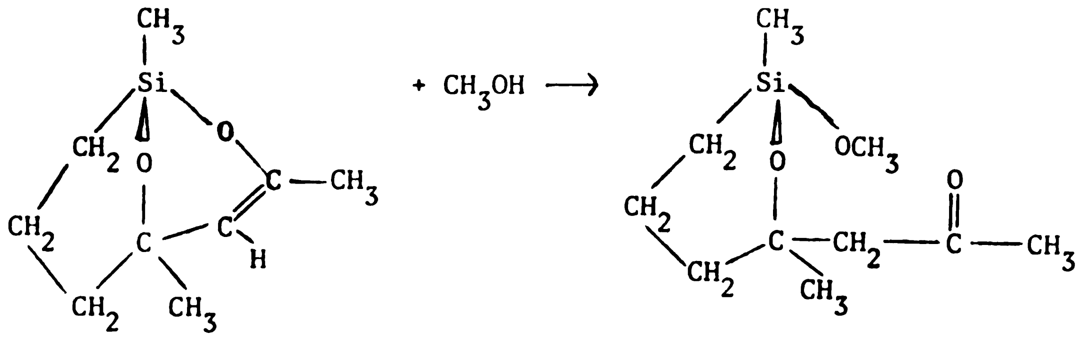

A
B
1800
1600
1400
CM-1

the $=CCH_3$ singlet at τ8.23, the $-CH_3$ doublet at τ8.79 and the =CH quartet at τ4.80. In the silyl enol ethers previously studied, the coupling between the =CH and allylic CH_3 protons was ∿0.4Hz or less and the coupling between =CH and $COCH_3$ protons was ∿0.6Hz.[37] The first step in the rearrangement of $CH_3Si(CH_2)_3(acac)$ must be a ring opening reaction. These ring-openings are catalyzed by trace amounts of HCl, H_2O, and a variety of other nucleophiles, and they may also be thermally induced.[38] Therefore, in successive preparations of $CH_3Si(CH_2)_3(acac)$ there was a large variation in the amount of rearrangement product observed, depending on the purity of the sample. Once the ring opens, it could attack the acac moiety by a Michael type addition illustrated below. To further verify the structure, the compound was allowed to react for 24 hours at room temperature with dry methanol, followed by removal of the methanol under reduced pressure. The nmr spectrum



illustrated in Figure 1 has a Si-OCH_3 line at ca., τ6.6 of intensity equal to the Si-CH_3 line at ca., τ9.95. The =CH line and the acac CH_3 lines are replaced by a line at τ7.6 and a complex multiplet at τ8.0. The solvolysis is illustrated in reaction 12. In general the reactivity of the Si-OR bond increases as the pK_a of the conjugate acid of -OR decreases.[39,40]

(12)



Nuclear magnetic resonance spectroscopy in conjunction with infrared spectroscopy confirms the structural similarity of the cyclic derivatives to acyclic $R_3Si(acac)$.[6] The lines observed in the nmr spectrum at ambient temperature are listed in Table VI. The acetylacetone moiety give rise to a =CH-proton multiplet near τ4.6 and a =CH- singlet near τ4.8, two methyl doublets near τ7.8 and τ8.0, and a methyl singlet near τ8.0. Si-CH_3 lines are present near τ9.6. The ring methylene protons exhibit a complex set of lines between τ8.5 and τ9.5. The presence of two =CH lines indicates the presence of cis and trans isomers. The acetylacetone lines near τ9.6, 8.0, 7.8 and 4.6 are to the cis isomers

Table VI. Proton Chemical Shift Data for *Cis* and *Trans* - Cyclic Organosilyl Acetylacetone Derivatives[a]

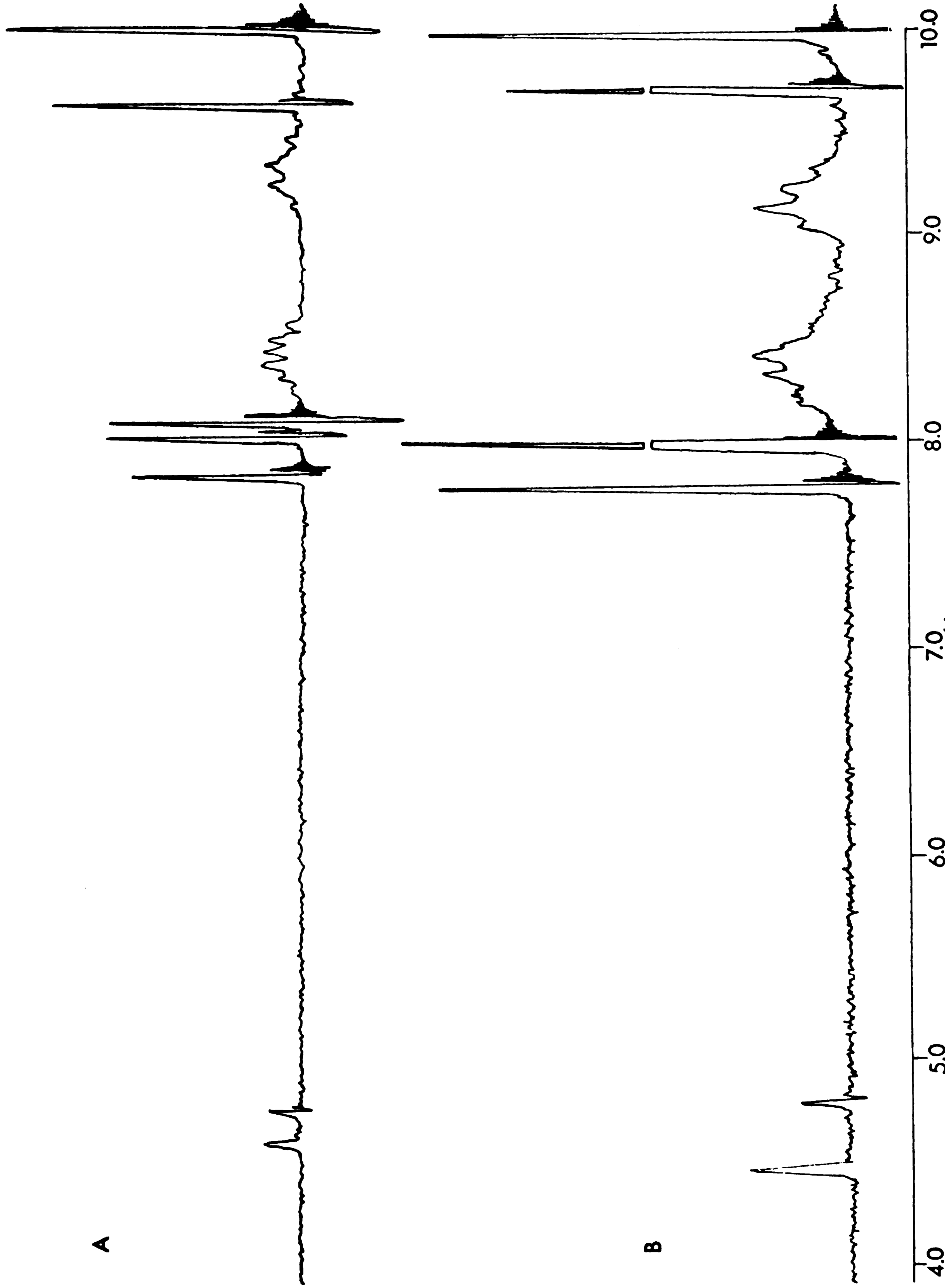
Compound	*Trans* Isomer				*Cis* Isomer		
	Si-CH_3	-CH_3	$COCH_3$	=CH-	Si-CH_3	CH_3[b]	=CH-
$CH_3Si(CH_2)_3(acac)$	9.58	7.99	7.75	4.70	9.63	8.08	4.82
$CH_3Si(CH_2)_4(acac)$	9.63	7.99	7.81	4.55	9.63	8.07	4.70
$CH_3Si(CH_2)_5(acac)$	9.73	8.00	7.80	4.48	9.73	8.00	4.82
$(CH_3)_3Si(acac)$[c]	9.74	8.00	7.82	4.53	9.74	8.03	4.81

a. All shifts reported as τ values; concentration is 25ml/100ml solvent; spectra in CCl_4 solution.

b. Time averaged methyl resonance.

c. Data for this compound taken from reference 6: concentration is 10 g/100 ml solvent.

Figure 3. Proton nmr spectra of A) $CH_3Si(CH_2)_4(acac)$ in CCl_4 (25 ml/100 ml solvent), B) $CH_3Si(CH_2)_5(acac)$ in CCl_4 (25 ml/100 ml solvent).


A
B
10.0
9.0
8.0
7.0
PPM(τ)
6.0
5.0
4.0

in accordance with the assignments made for $(CH_3)_3Si(acac)$.[37] The single acac methyl line in the _cis_ isomer arises from rapid rearrangement, which will be discussed in section III E. The Si-CH_3 lines of the _cis_ and _trans_ isomers are accidentally coencident at ambient temperature, but can be resolved in each case as the temperature is lowered. Separation of _cis_ and _trans_ - $(CH_3)_3Si(acac)$ by gas chromatography and distillation through a spinning band column was unsuccessful, suggesting a rapid equilibrium between the isomers.[37] Facile isomerization is supported by the fact that the same _cis_ to _trans_ ratio's were observed for samples of acyclic $R_3Si(acac)$ derivatives immediately after distillation, and after ageing for 6 months at room temperature.[27] $CH_3Si(CH_2)_4(acac)$ and $CH_3Si(CH_2)_5(acac)$ were allowed to age for 2 days before determining the _cis_ to _trans_ ratio, but the _cis_ to _trans_ ratio of $CH_3Si(CH_2)_3(acac)$ was determined immediately after distillation.

The _cis_ to _trans_ ratios shown in Table VII were determined by planimetric integration of the =CH lines. After the samples had aged 2 months at room temperature, the _cis_ to _trans_ ratios of the compounds remained constant. The amount of _cis_ isomer observed increases as the ring size decreases, with a large increase in _cis_ isomer observed for the four member ring compound. The magnitude of the change in the amount of _cis_ isomer due to ring size is much greater than that observed due to inductive effects of silyl substituents (_cf._, Table III). The data suggest a relationship between ring strain and the strength of the incipient silicon-oxygen interaction.

Table VII. Equilibrium Ratio of Cis and Trans Enol Ether Isomers for $CH_3Si(CH_2)_x$ Derivatives of Acetylacetone.[a]

Compound	[cis]/[trans]
$CH_3Si(CH_2)_3$(acac)	2.23
$CH_3Si(CH_2)_4$(acac)	0.45
$CH_3Si(CH_2)_5$(acac)	0.25
$(CH_3)_3Si$(acac)[b]	0.34

a. In carbon tetrachloride at ambient temperature; concentration is 25 ml/100 ml of solvent.

b. Value for this compound was taken from reference 6; the solvent is chlorobenzene; concentration is 0.6 m.

The structure of silacycloalkanes have been studied by electron diffraction.[41-43] The ring in silacyclobutane is highly puckered to allow adjacent CH_2 groups to be staggered. The relative importance of angle strain in the carbon skeleton is lessened due to the deformation of the C-Si-C angle. Silacyclobutane and dichlorosilacyclobutane both were studied and found to have C-Si-C angles of 80°. The exocyclic angle was 109° and 105°, respectively.[41] The deformation of the C-Si-C angle causes an alteration of the hybrid character, as determined by the exocyclic Si-H infrared stretching frequencies. There is an increased amount of s character to the exocyclic bonds.[38] The amount of ring strain in silacyclopentane is not as great as the strain present in the four-member ring.[35] The ring is bent and the C-Si-C angle is 96°.[43] The six member ring in 1,3,5-trisilacyclohexane has C-Si-C angles of 109.5° and adopts the chair conformation.[43] Relief of ring strain by incipient pentacoordination and distortion towards a trigonal bipyramid ground state would strengthen the silicon-oxygen interaction in the four and five member ring compounds. This effect is greatest for the four member ring. The reluctance of the six member ring compound to distort its tetrahedral angles is illustrated by the smaller amount of cis isomer relative to the acyclic derivative.

Selective vibrational frequencies for the cyclic organosilyl acetylacetone derivatives are reported in Table VIII. The frequencies observed are in good agreement with the previously reported values for acyclic $R_3Si(acac)$ compounds.[6] The compounds all have a strong band

Table VIII. Infrared Absorbtion Bands for Cyclic Organosilyl Acetylacetone Derivatives.[a]

Compound	γ C=O	γ C=C	Si-O
$(CH_3)_3$Si(acac)[b]	1678(1659)[c] cm^{-1}	(1625)1588 cm^{-1}	1032 cm^{-1}
$CH_3Si(CH_2)_3$(acac)[d]	(1677)1662 cm^{-1}	(1622)1589 cm^{-1}	1044 cm^{-1}
$CH_3Si(CH_2)_4$(acac)	1680 cm^{-1}	(1625)1589 cm^{-1}	1044 cm^{-1}
$CH_3Si(CH_2)_5$(acac)	1678 cm^{-1}	(1620)1587 cm^{-1}	1042 cm^{-1}

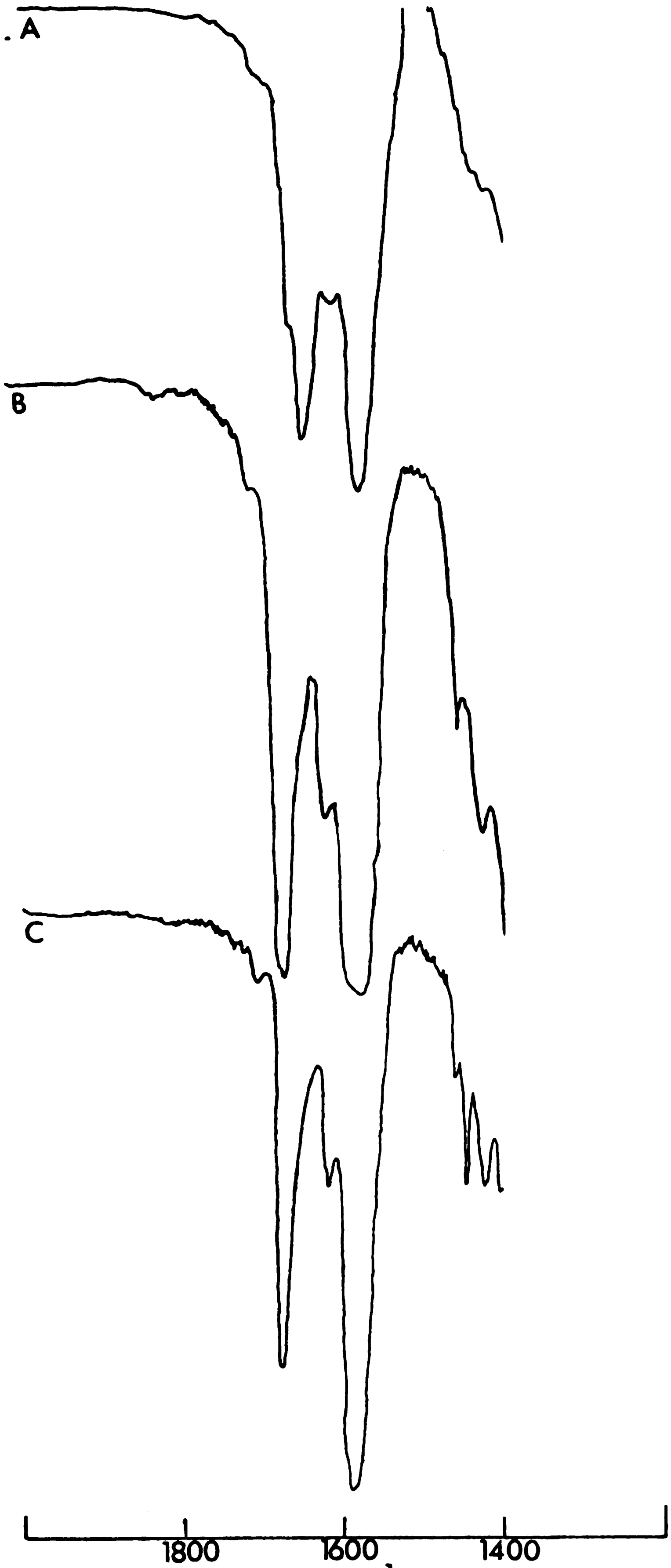
a. In carbon tetrachloride unless otherwise stated; concentration is 5ml/100ml solvent.

b. Data for this compound were taken from reference 6.

c. Weak bands or shoulders are given in parentheses.

d. Frequencies for this compound were recorded in dichloromethane.

Figure 4. Infrared spectra in the region 1800-1400 cm^{-1} for A) $CH_3Si(CH_2)_3$(acac) in CH_2Cl_2 (5 ml/100 ml solvent), B) $CH_3Si(CH_2)_4$(acac) in CCl_4 (5 ml/100 ml solvent) C) $CH_3Si(CH_2)_5$(acac) in CCl_4 (5 ml/100 ml solvent).


A
B
C
1800
1600
1400
CM^{-1}

between 1600-1700 cm^{-1} corresponding to the uncoordinated carbonyl stretching frequency. For $(CH_3)_3Si(acac)$ the band at 1678 cm^{-1} is assigned to the trans isomer with the shoulder at 1659 cm^{-1} assigned to the cis isomer.[44] In the silacyclobutane derivative, the higher energy C=O stretch of the trans isomer appears as a shoulder on the strong 1662 cm^{-1} band of the cis isomer. The C=O stretch of the cis isomers of $CH_3Si(CH_2)_4(acac)$ and $CH_3Si(CH_2)_5(acac)$ is not resolved from the C=O vibration of the trans isomer. The presence of a Si-O group in each compound is indicated by a strong band in the region 1000-1050 cm^{-1}. The strong band at ca., 1589 cm^{-1} is attributed to the C=C vibration. The intensity of this band is enhanced by conjugation with the carbonyl group.[34.36] It has been suggested that the incipient silicon-oxygen interaction should cause a shift in the carbonyl vibrational frequency to lower frequencies. The C=O band in α-ketosilanes is shifted 68-70 cm^{-1} to longer wavelengths relative to their carbon analogues, and in β-ketosilanes the band is shifted 19 cm^{-1}. The C=O stretch of δ-ketosilanes is not shifted relative to their carbon analogues.[45,46] It has been suggested that the 18 cm^{-1} low energy shift in the C=O stretch of $(CH_3)_3Si(tropolone)$, relative to free tropolone may be due to incipient pentacoordination in the silyl derivative.[9] An infrared study of several trimethylsilyl derivatives of ligands where incipient pentacoordination may be anticipated[44] led Sommer[2] to the conclusion that no incipient silicon-oxygen interaction was occurring. Included in this study was $(CH_3)_3Si(acac)$. The cis and trans carbonyl bands for $(CH_3)_3Si(acac)$ and for the analogous methyl enol ether are reported equal.[44] Variations in the extent of incipient pentacoordination in silyl enol ethers as reflected by cis to trans ratios does not correlate with their relative C=O stretching frequencies. For example, the C=O band in cis- $(CH_3)_3Si(acac)$ is at 1659 cm^{-1} and at 1662 cm^{-1} for $CH_3Si(CH_2)_3(acac)$. The shift is small and in a direction opposite to that which would be predicted on the basis of the cis to trans ratios.

B. Preparation and Characterization of $(CH_3)_3Si(hfac)$ and $(CH_3)_3Si(dpm)$

Trimethylsilylhexafluroacetylacetone $(CH_3)_3Si(hfac)$, prepared by the reaction of neat trimethylchlorosilane and hexafluroacetylacetone (Equation 13). Trimethylsilyldipivaloylmethane, $(CH_3)_3Si(dpm)$, was

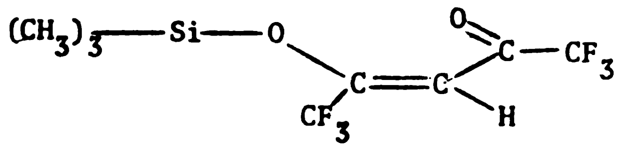
$$(13) \qquad (CH_3)_3SiCl + H(hfac) \rightarrow (CH_3)_3Si(hfac) + HCl$$

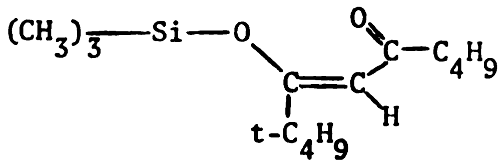
prepared by the reaction of trimethylchlorosilane and sodium salt of dipivaloylmethane in hexane (Equation 14). A related compound,

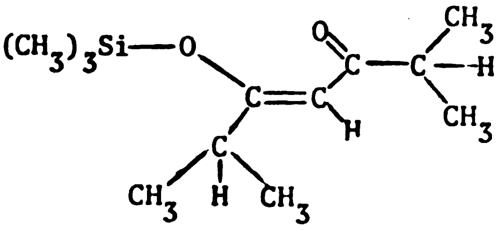
$$(14) \qquad (CH_3)_3SiCl + Na(dpm) \rightarrow (CH_3)_3Si(dpm) + NaCl$$

trimethylsilyldiisobutylmethane was prepared by Alan Schwartz by the same method used to prepare $(CH_3)_3Si(dpm)$. The compounds were colorless to pale yellow liquids. They are hydrolyzed on contact with moist air.

The nmr spectrum of $(CH_3)_3Si(hfac)$ exhibits a single $Si\text{-}CH_3$ line at τ9.65 and a single =CH- line at τ3.70. The F^{19} nmr spectrum showed two sharp lines of equal intensity assigned to the two non-equivalent CF_3 groups in the trans isomer. The chemical shift difference between the fluorine lines is proportional to the magnetic field strength (442.5 Hz at 94.6 MHz and 260.0 Hz at 56.4 MHz), which indicates that the two lines are singlets and not an anomalous doublet.[27] The nmr spectrum of $(CH_3)_3Si(dpm)$ exhibits a singlet $Si\text{-}CH_3$ line at τ9.65 and a single =CH- line at τ3.70. The t-butyl groups on dipivaloylmethane gave rise to a single resonance at τ8.91. The presence of only one t-butyl line is


$(CH_3)_3Si(hfac)$


$(CH_3)_3Si(dpm)$


$(CH_3)_3Si(dibm)$

attributed to the presence of only the cis isomer, which is undergoing a rapid stereochemical rearrangement (cf., section IIIE). The nmr spectrum of $(CH_3)_3Si(dibm)$ exhibits lines characteristic of both cis and trans isomers.[47] On comparison of the cis to trans ratios to trimethylsilylacetylacetone, we find that as the methyl is replaced by the more electron releasing isopropyl group the cis to trans ratio increases from 0.34 to 0.55 (Table IX). A further increase in electron releasing ability by replacement with t-butyl groups results in only the cis isomer

Table IX. Equilibrium Ratios of Enol Ether Isomers for Trimethylsilyl-β-diketonates.[a]

Compound		[cis]/[trans]
$(CH_3)_3Si(hfac)$	$R = CF_3$	< 0.02
$(CH_3)_3Si(acac)$[b]	$R = CH_3$	0.34
$(CH_3)_3Si(dibm)$	$R = CH(CH_3)_2$	0.55
$(CH_3)_3Si(dpm)$	$R = C(CH_3)_3$	>50.0

a. In carbon tetrachloride at ambient temperature, concentration is 25 ml/100 ml solvent.

b. Data for this compound were taken from reference 37; solvent is chlorobenzene; concentration is 0.60 m.

being observed by nmr spectroscopy. Steric effects, especially in the case of _t_-butyl groups, should favor the _cis_ isomer. Steric effects, however, do not influence the _cis_ to _trans_ ratio of the hexafluroacetylacetone derivative where only the _trans_ isomer is observed. It is probable that the electrostatic interaction between silicon and the uncoordinated oxygen is important in determing these _cis_ to _trans_ ratios.

The infrared spectrum of $(CH_3)_3Si(hfac)$ exhibits a single C=O stretching frequency at 1733 cm^{-1}, a C=C stretching frequency at 1625 cm^{-1}, and a Si-O stretch at 945 cm^{-1}. $(CH_3)_3Si(dpm)$ exhibits a single C=O stretch at 1676 cm^{-1}, a C=C stretch at 1625 cm^{-1}, and a Si-O stretch at 1100 cm^{-1}. The presence of only one C=O frequency in each case is attributed to the $(CH_3)_3Si(hfac)$ existing exclusively as the _trans_ isomer and to $(CH_3)_3Si(dpm)$ as the _cis_ isomer. It has been suggested that the variation in the Si-O vibrational frequency from the normal range of 1000-1050 cm^{-1}, is due to the inductive effects of the CF_3 and _t_-butyl groups on the Si-O bond strength.[27]

C. Preparation and Characterization of $(C_6H_5CH_2)(CH_3)(C_6H_5)Si(dpm)$

In an effort to synthesize a compound in which diastereotopic environments could be observed in the proton nmr spectrum, several different chiral triorganochlorosilanes were prepared. The chlorosilanes were prepared by the reaction of methylphenyldichlorosilane and the appropriate Grignard reagent. The chlorine was replaced with acac or dpm as described previously. Compounds of the type $R(CH_3)(C_6H_5)Si(acac)$

were prepared where R was equal to 2-propanol, 2-d-2-propanol,[48] 2,6-dimethylphenyl; and benzyl groups. When R was a benzyl group, it appeared that the diastereotopic methylene protons were present in the nmr spectrum, but they overlapped with the acac methyl lines. The deuterated acac derivative,[49] $(C_6H_5CH_2)(C_6H_5)Si(acac\text{-}d_7)$, provided a better resolved methylene pattern, but the spectrum was still complex due to the presence of cis and trans isomers. The nmr spectrum of $(C_6H_5CH_2)(CH_3)(C_6H_5)Si(dpm)$ is simplified by the presence of only the cis isomer. The compound was prepared as illustrated in equations 15 and 16.

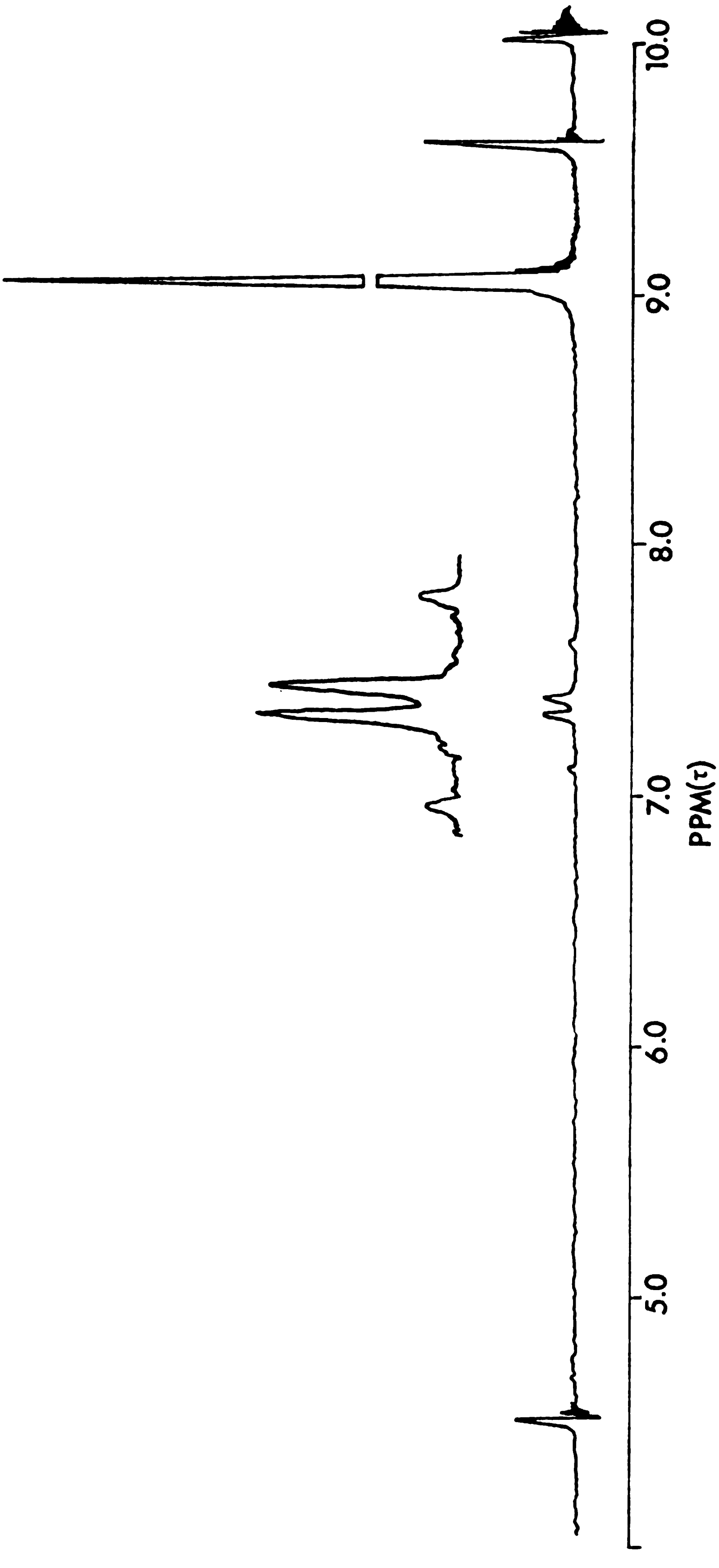
$$(15)\quad C_6H_5CH_2\text{-}Mg\text{-}Cl + (CH_3)(C_6H_5)SiCl_2 \rightarrow MgCl_2 + (C_6H_5CH_2)(CH_3)(C_6H_5)SiCl$$

$$(16)\quad (C_6H_5CH_2)(CH_3)(C_6H_5)SiCl + Na(dpm) \rightarrow (C_6H_5CH_2)(CH_3)(C_6H_5)Si(dpm) + NaCl$$

The compound was a pale yellow viscous liquid that hydrolyzed in contact with moist air. After ageing for over a year at room temperature, the compound remained unchanged, as judged from nmr spectroscopy.

The nmr spectrum of cis-$(C_6H_5CH_2)(CH_3)(C_6H_5)Si(dpm)$ contains a Si-CH_3 line at τ9.56, a t-C_4H_9 line at τ9.00 and a =CH-line at τ4.30. The C_6H_5 multiplets are centered near τ3.0. The benzyl methylene protons are diastereotopic and exhibit an AB pattern centered at τ7.23 ($\Delta\nu$ = 11.0 Hz, J = 13.5 Hz). The spectrum is illustrated in Figure 5. The intensity ratio of the central to the outer bands of the AB pattern is calculated to be 7.8:1, which agrees with the experimentally determined ratio.

Figure 5. Proton nmr spectra of A) $(C_6H_5CH_2)(CH_3)(C_6H_5)Si(dpm)$ in CCl_4 (25 ml/100 ml solvent), B) Benzyl methylene proton AB pattern in CCl_4 (50 ml/100 ml solvent).

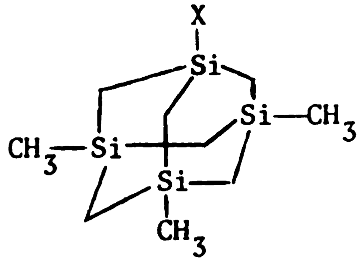

10.0
9.0
8.0
7.0
6.0
5.0
PPM(τ)

The infrared spectrum exhibits a carbonyl stretching band at 1675 cm^{-1}, a C=C stretch at 1600 cm^{-1} and a Si-O stretch at 1100 cm^{-1}. The spectrum is similar to that obtained for $(CH_3)_3Si(dpm)$.

D. Attempted Preparation of 1,3,5,7-tetrasilaadamantane Derivative

The tetrasilaadamantane cage is prepared from 1,1,3,3,5,5-hexamethylsilacyclohexane by a ligand redistribution reaction catalyzed by $AlCl_3$ (Equation 17). The $AlCl_3$ also acts as a reactant, giving rise to chlorine in place of a methyl group. Massive amounts of $AlCl_3$, between 20-200% of the $[CH_2Si(CH_3)_2]_3$ weight, is used to produce facile redistribution at a moderate temperature.[31] Frye purified the silaadamantanes by preparative glc. However, in the present work vacuum sublimation at room temperatures provided an easy purification route. Although fractional sublimation of the tetramethyl and trimethyl-chloro adamantanes appeared possible, the mixture was used without further purification.

(17) $2[CH_2Si(CH_3)_2]_3 \xrightarrow{AlCl_3} 2(CH_3)_4Si +$



The 1,1,3,3,5,5-hexamethyl 1,3,5-trisilacyclohexane required as a starting reagent was prepared from chloromethyldimethylchlorosilane by a Grignard reaction (Equation 18).

$$(18) \quad (ClCH_2)(CH_3)_2SiCl + Mg \rightarrow [CH_2Si(CH_3)_2]_3 + MgCl_2$$

The tetramethyl and trimethylchloroadamantes were identified by nmr spectroscopy and infrared spectroscopy.[32] The nmr spectrum of the sublimed crystals exhibited lines at τ9.74, τ9.83 and τ10.22 that are charactertistic of the silaadamantane with one Si-Cl functional group. The presence of the tetramethyladamantane was indicated by lines at τ9.90 and τ10.28. The infrared spectrum contained characteristic bands at 527 cm^{-1}, 1027 cm^{-1}, and 1248 cm^{-1}, corresponding to Si-Cl, $Si\text{-}CH_2\text{-}Si$, and $Si\text{-}CH_3$ frequencies, respectively. As an additional check for the Si-Cl functional group, AgCl was precipitated from a nitric acid solution of the crystals.

The purpose of preparing the silaadamantane was to determine whether a reaction between the Si-Cl functional group and a β-diketone was possible and whether the product would undergo an intramolecular rearrangement. The mixture of silaadamantanes was allowed to react with the sodium salt of dpm in CCl_4 and also with Hacac and pyridine in CCl_4. The reactions were followed by nmr spectroscopy. After a reaction time of one week at room temperature, the adamantane-Na(dpm) mixture gave rise to a new nmr line at τ9.93, in addition to the original silaadamantane lines. The reaction with Hacac and pyridine also gave rise to a product exhibiting in τ9.93 line, but no lines characteristic of the acac moiety were present. Thus neither reaction mixture provided evidence of the desired product. The reaction of β-diketones and chlorosilanes proceeds with inversion of configuration,[24] probably involving backside attack. The silaadamantane cage structure blocks a backside approach.

E. Kinetic Study of the Intramolecular Rearrangement of *cis*-triorganosilyl-β-diketone Derivatives

The temperature dependence of the nmr spectrum of the compounds prepared for this study was attributed to an intramolecular rearrangement involving migration of the silyl group between the two oxygens in the β-diketone (see Eq. 6). The rate of the rearrangement was calculated by the simplified Gutowsky-Holm equation for the coalescence of singlets (Equation 19).[50] The simplified equation is based on the assumption that $\tau_A = \tau_B$ and $T_2\Delta\nu$ is large. The general validity of the approximate equations have been tested by a comparison to complete line shape analysis.[51,52] Values for k_c obtained by complete line shape analysis for equally intense coalescing singlets or doublets are within 6% of the rate obtained using the approximate equation, when $\Delta\nu$ is 20 Hz.[51] An error of 6% for k_c will result in an error for $\Delta G^{\ddagger}$ of less than 0.1 kcal/mole at the coalescence temperature. The value of $\Delta\nu$ for the silyl dipivaloylmethane derivative was taken to be equal to the limiting frequency separation in the region of slow exchange. The frequency separations at the coalescence temperatures for the acac derivatives were extrapolated from the temperature dependences of $\Delta\nu$ in the region of slow exchange. The activation free energies were

$$\frac{1}{\tau_A} = k_c = \left(\frac{\pi}{\sqrt{2}}\right)\Delta\nu \tag{19}$$

where τ_A is the mean lifetime (sec) of a proton at site A

k_c is the rate constant (sec^{-1}) calculated at the coalescence temperature

$\Delta\nu$ is the frequency separation (Hz) in the absence of exchange calculated from Equation 20.

$$(20) \qquad k = \frac{RT}{Nh} \exp \left(\frac{-\Delta G^{\ddagger}}{RT}\right)$$

The interchange of non-equivalent methyl groups in cis-$R_3Si(acac)$ derivatives (cf., Table IV), is sufficiently slow to permit observation of two well resolved methyl proton resonance lines below -40°. As the temperature is raised the two lines broaden and merge into a very broad line, which then sharpens above the coalescence temperature. The activation parameters for the rearrangement of cis-$(CH_3)_3Si(acac)$ have been previously determined by line broadening analysis.[6] A first order rate constant of 851 sec^{-1}, an activation energy of 13.8 ± 0.5 kcal/mole and an activation entropy of -0.8 ± 2.5 e.u. were found at 25°.

$(CH_3)_3Si(dpm)$ rearranged at a much greater rate than the corresponding acac derivative. In ClF_2CH solution the t-butyl line remained sharp even at -137°. A lower limit to the first order rate constant was estimated based on the $\Delta\nu$ observed in the region of slow exchange for $(C_6H_5CH_2)(CH_3)(C_6H_5)Si(dpm)$. At -137°, $\Delta G^{\ddagger}$ for $(CH_3)_3Si(dpm)$ is <6.7 kcal/mole. If one assumes $\Delta S^{\ddagger}$ is zero, as in the case of $(CH_3)_3Si(acac)$, then $k_{25°}$ is >7.76 10^7 sec^{-1}. At the estimated coalescence temperature (-95°) for $(CH_3)_3Si(dpm)$, $\Delta G^{\ddagger}$ is less than 9.4 kcal/mole. $(CH_3)_3Si(hfac)$ exhibits only the trans isomer which is stereochemically ridged at temperatures up to 40°C. These results show that when the methyl group on the β-diketone is replaced by an isopropyl or a t-butyl group, the activation free energy for the rearrangement decreases, by at least 4 and 7 kcal/mole, respectively. This decrease is most likely due to an increase in electron density at the uncoordinated carbonyl oxygen. The magnitude of the effect is comparable to the effect of substitution on pyrazole in the rearrangement of $(CH_3)_3Si(pyrazole)$[10] (cf., Table IV), and supports the importance of the long range electrostatic interaction between the silicon and the uncoordinated carbonyl oxygen.

Figure 6 illustrates the possible reaction pathways and the stereochemical result of each path. Attack by the uncoordinated oxygen at an opposite tetrahedral edge will result in an intermediate in which the diketonate spans two equatorial positions. This structure is unfavorable because two electronegative atoms are in equatorial positions[4] and because of the O-Si-O bond angle of 120°. Lingafelter and Braun have shown that acac normally assumes an O-M-O bond angle of 90°.[53] Attack at an opposite edge lead to inversion of configuration at silicon. Attack of the uncoordinated oxygen at an adjacent tetrahedral edge or face will result in an intermediate with the diketonate spanning axial equatorial position, and will result in retention of configuration at silicon. Pseudorotation using an R group as a pivot will not alter the stereochemical result of the latter intermediate, however use of an oxygen as a pivot will interchange the two intermediates.

The stereochemical consequences of the rearrangement process was determined by an nmr investigation of the chiral compound cis-$(C_6H_5CH_2)(CH_3)(C_6H_5)Si(dpm)$. The temperature dependence of the nmr spectrum is illustrated in Figure 7. The t-butyl groups are resolved into two lines of equal intensity below -100°. The lines coalesce at -88.4 and sharpen to a single peak at -60°. The AB pattern of the benzylmethylene protons is retained in the region of fast exchange indicating

Figure 6. Mechanisms which would account for the exchange of the non-equivalent R groups of a β-diketone in *cis*-R_3Si (β-diketone).

nge of the

is-R_3Si

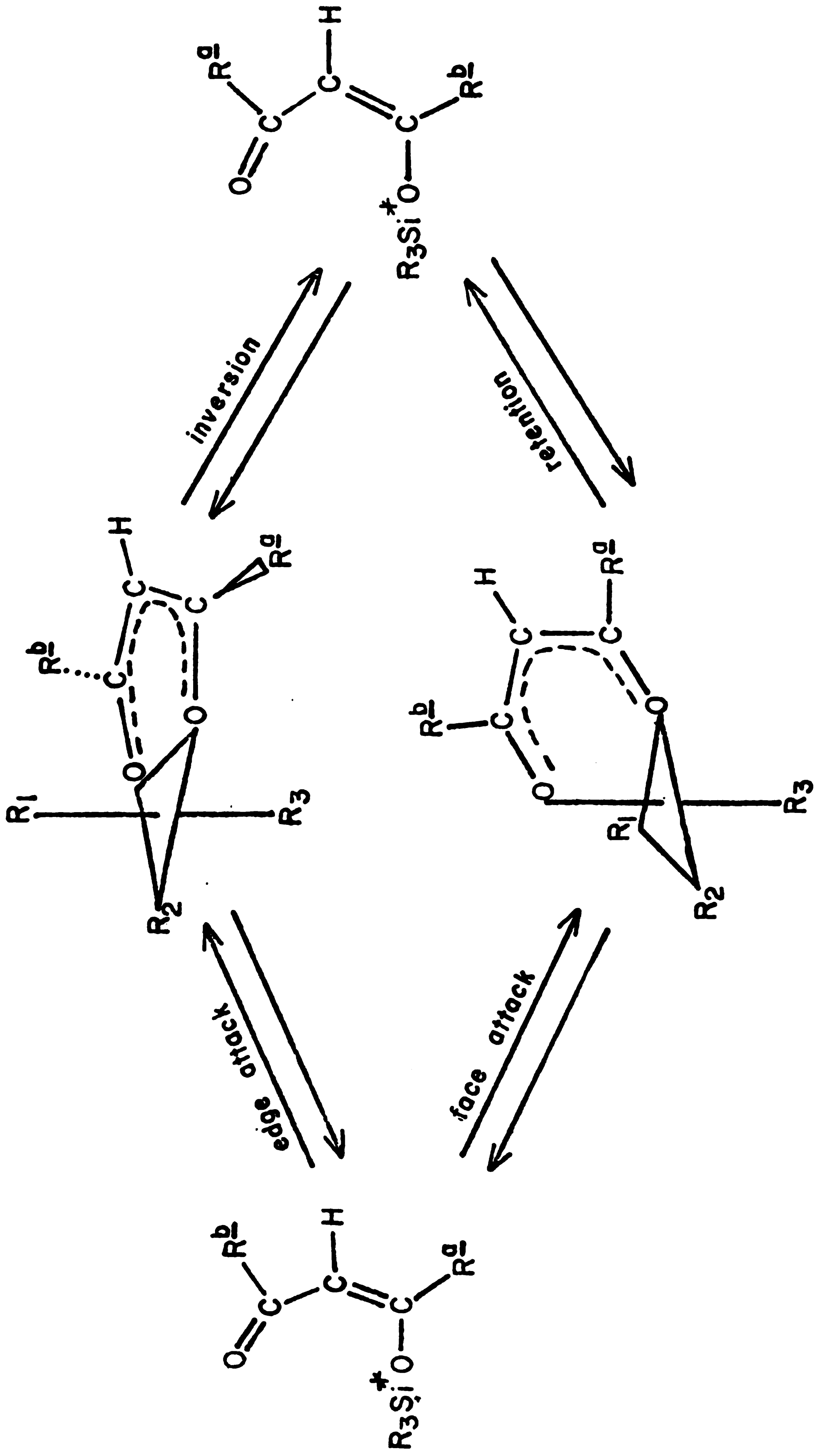
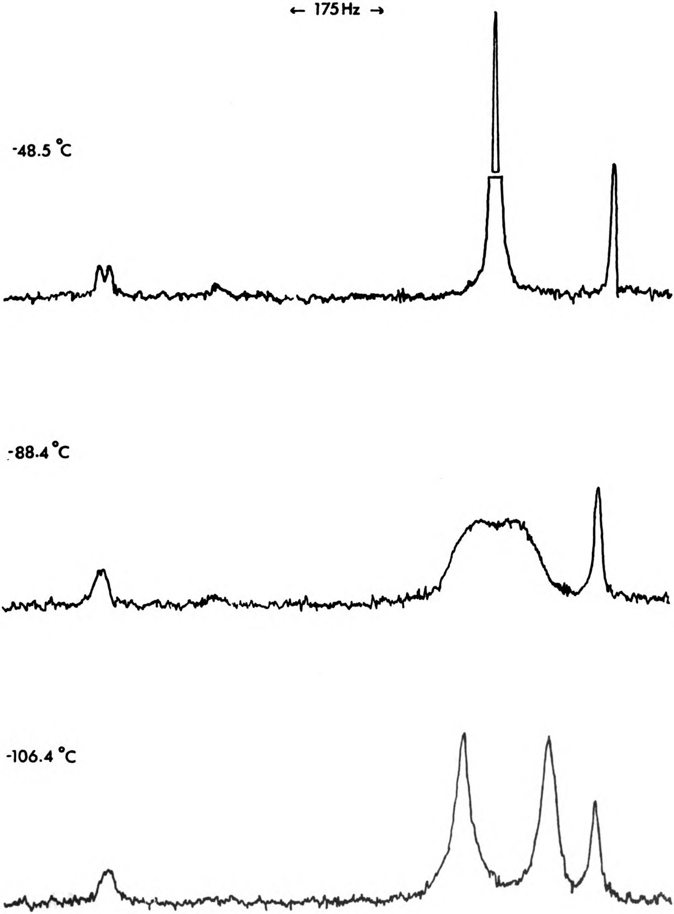
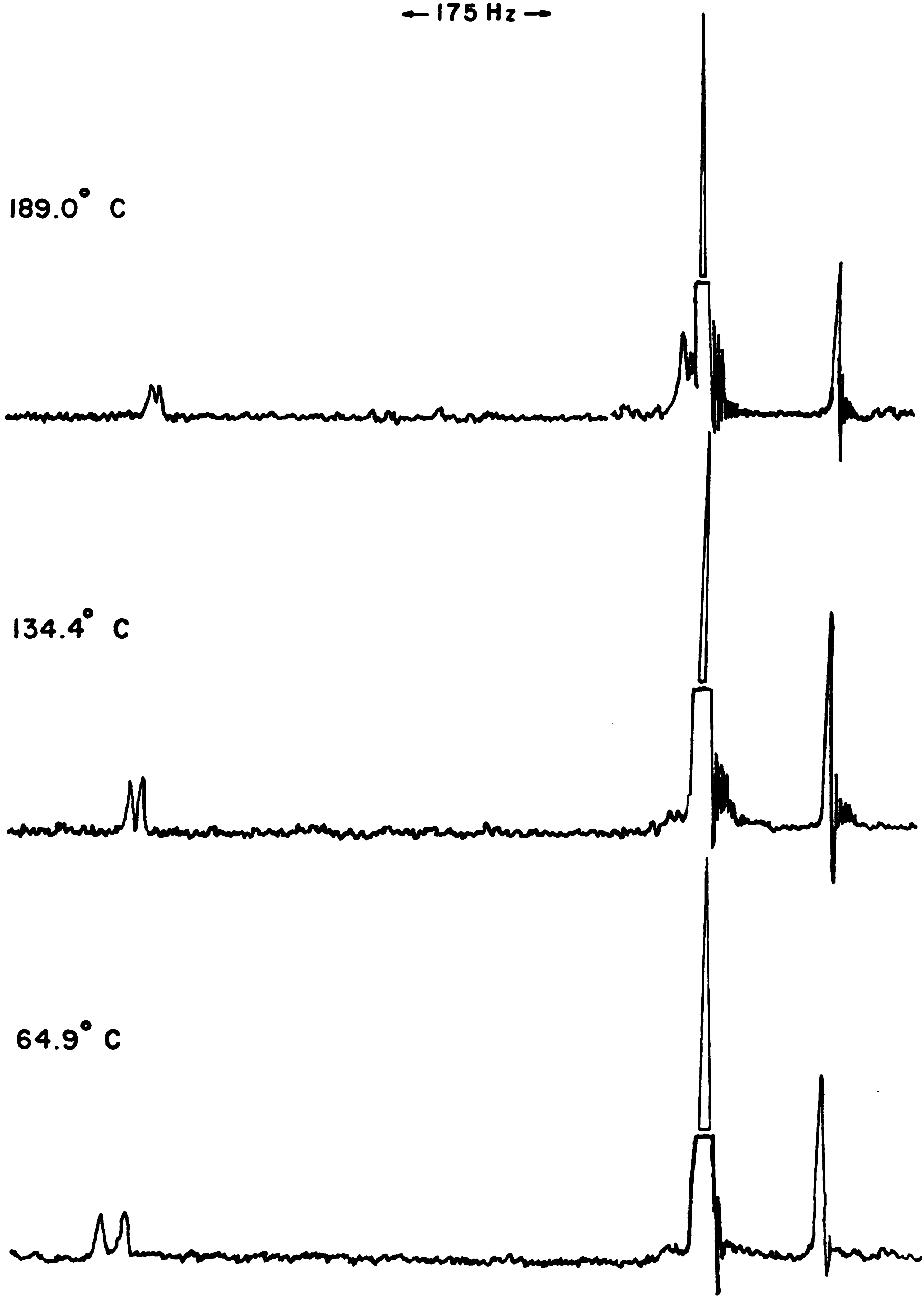


Figure 7. Temperature dependence of the proton nmr spectrum of $(C_6H_5CH_2)(CH_3)(C_6H_5)Si(dpm)$ low temperature spectra were recorded in ClF_2CH (12.5 ml/100 ml solvent) high temperature spectra were recorded in chloronaphthalene (12.5 ml/100 ml solvent).


← 175Hz →
-48.5 °C
-88.4 °C
-106.4 °C


← 175 Hz →
189.0° C
134.4° C
64.9° C

retention of configuration. From these data the first order rate constant for the retention rearrangement process at 25° is 1.1×10^6 sec^{-1} and the activation free energy is 9.2 kcal/mole. The AB pattern of the benzyl methyl protons persisted to a temperature of 211°C, although the separation between the central bands decreases, causing the two outer bands of the multiplet to dissappear. At 211° the inversion process is not yet observed. A lower limit to the first order rate constant for the inversion process was estimated from the simplified Gutowsky-Holm equation. Equation 21 for coupled AB spin systems is only accurate when

$$(21) \qquad k_c = \left(\frac{\pi}{\sqrt{2}}\right)(\Delta\nu^2 + 6J^2)^{1/2}$$

$\Delta\nu > J$. Equation 19 is more accurate for small $\Delta\nu$ values. The value of $\Delta\nu$ at 211° was estimated to be 3.6 Hz.

The estimate was based on the known coupling constant at ambient temperatures and the observed frequency separation at 211°C, along with the fact that the intensity ratio of the central to the outer bands must be greater than 10:1. The relationship between the intensity ratio and observed frequency separation between the bands (I_c/I_o = $(\nu_1 - \nu_4)/(\nu_2 - \nu_3)$ where ν_1 and ν_4 are outer bands) may be used to calculate $\Delta\nu$. The first order rate constant was estimated to be $<1.5 \times 10^{-7}$ at 25° and $\Delta G^{\ddagger}$ is >27 kcal/mole. The difference in $\Delta G^{\ddagger}$ between the retention and inversion process is >18 kcal/mole. Similar data have recently been reported for the R_3Si(acac) rearrangement and R_3Si(tropolone) rearrangements studied by C^{13} nmr spectroscopy,[9] where differences between the retention and inversion processes of >9.2 kcal/mole and >9.9 kcal/mole, respectively, were found. The lower limit for the difference in

$\Delta G^{\ddagger}$ values for inversion and retention processes of $(C_6H_5CH_2)(CH_3)(C_6H_5)Si(dpm)$ is >17.8 kcal/mole. At 25°, the ratio of rate constants for rearrangement and inversion is at least 1:0.79 x 10^{13}. Fewer than one rearrangement out of every 10^{13} results in inversion of configuration. Space filling models of $(C_6H_5CH_2)(CH_3)(C_6H_5)Si(dpm)$ indicate a great deal of steric hinderance between the bulky phenyl groups and the dipivaloylmethane. This factor is probably important in the large difference in observed rates of rearrangement between $(CH_3)_3Si(dpm)$ and $(C_6H_5CH_2)$-$(CH_3)(C_6H_5)Si(dpm)$.

The cis-cyclic organosilyl acetylacetone derivatives exhibited a single methyl resonance at ambient temperatures (see Figures 1 and 3). As the temperature was lowered the methyl line broadened and was resolved into two lines of equal intensity below -40° and -100° for the six member and the five member ring compounds, respectively. The temperature dependence of the nmr spectrum of the silacyclohexane derivative is illustrated in Figure 8. The methyl resonance in the four-member ring compound was still sharp at -142°, at which point the compound was no longer soluble in ClF_2CH. The compound redissolved on warming to give a normal spectrum. The estimated first order rate constants and the activation free energies are listed in Table X. The rearrangement rate at 25° increased by three orders of magnitude when the six member ring was replaced by a five membered ring. A further increase in $k_{25°}$ of at least two orders of magnitude was observed for the four-membered ring compound. The effect of increasing the ring strain is to increase the reactivity of the compound towards

Figure 8. Temperature dependence of the proton nmr spectrum of $(CH_2)_5Si(CH_3)(acac)$ in CH_2Cl_2 (12.5 ml/100 ml solvent).

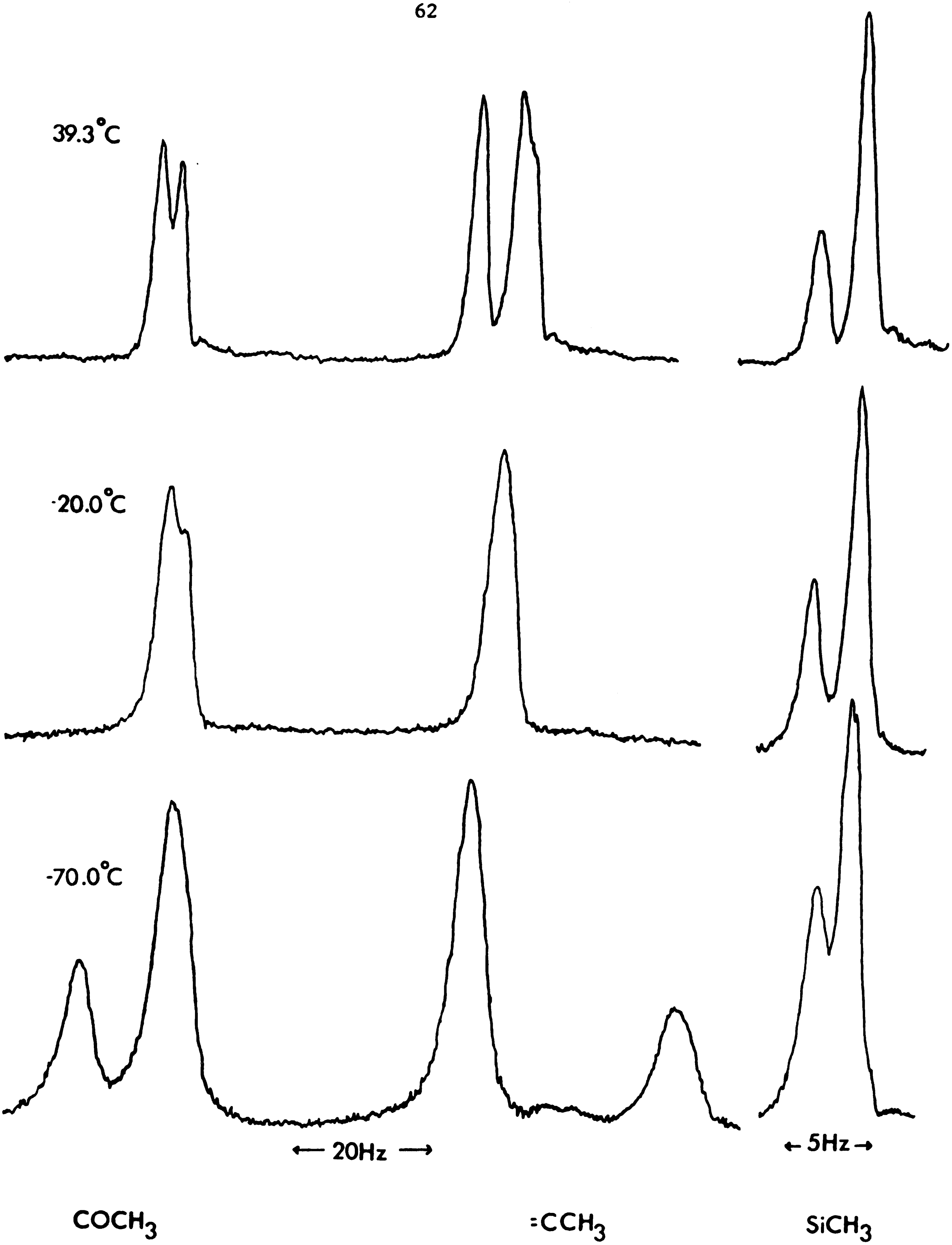

39.3°C
-20.0°C
-70.0°C
← 20Hz →
← 5Hz →
COCH$_3$
=CCH$_3$
SiCH$_3$

Table X. **Kinetic Data for the Intramolecular Rearrangement of** <u>cis</u>-**Cyclic Organosilyl Acetylacetone Derivatives**[a]

Compound	T_c(°C)	$\Delta\nu_o$,Hz	k_{Tc},sec^{-1}	$k_{25°}$,sec^{-1} [d]	$\Delta G^{\ddagger}$,Kcal/$mole^{-1}$ [e]
$CH_3Si(CH_2)_3$(acac)	<-142°	17.15[b]	38.1	$>1.05\times10^{8}$	<6.5
$CH_3Si(CH_2)_4$(acac)	-88.8°	17.16	38.1	9.82×10^{5}	9.3
$CH_3Si(CH_2)_5$(acac)[c]	-20.0°	17.14	38.1	2.16×10^{3}	12.9
$(CH_3)_3Si$(acac)	----	----	----	851	13.8

a. In ClF_2CH unless otherwise stated, concentration is 12.5 ml/100 ml solvent.

b. Assumed value.

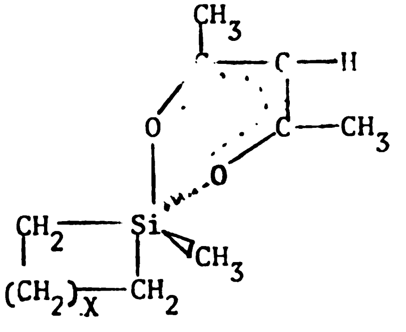
c. In CH_2Cl_2, concentration is 12.5 ml/100 ml solvent.

d. Calculated from Eyring equation.

e. Extrapolated value at 25°.

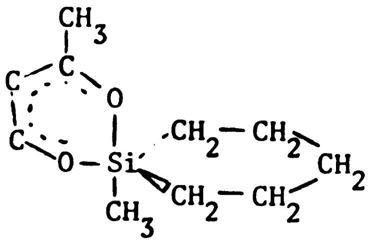
nucleophilic attack by the uncoordinated oxygen. The decrease in the activation free energy may be attributed to the release of ring strain by formation of a five coordinate intermediate. The rate of hydrolysis of cyclic organosilanes have been reported to increase from a relative rate of 0.1 for the six member ring compound to 10 for the five member ring compound and to 10,000-100,000 for the four member ring compound.[54-56] The effects of ring strain on the reactivity of silicon compounds is analogous to ring strain effects on tetravalent phosphorous.[3,57,58]

The most probable intermediate in the rearrangement of cis-$CH_3Si(CH_2)_3$(acac) and cis-$CH_3Si(CH_2)_4$(acac) is illustrated below. Electronegative atoms normally occupy axial positions and four and



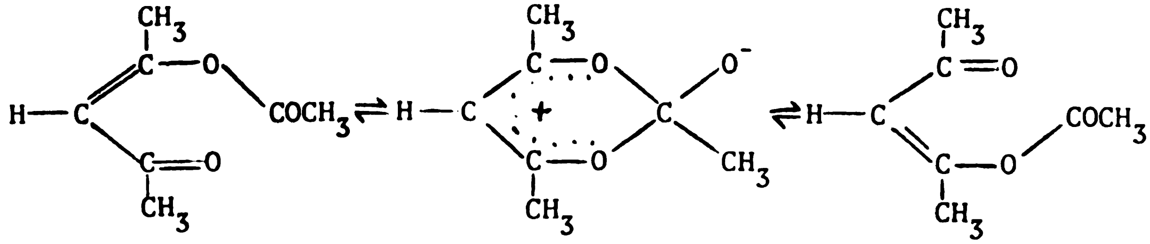
where x = 1 or 2

five member rings span axial-equatorial positions.[4,57] The acac is shown spanning an axial-equatorial position. The six member ring compound exhibits a rate of rearrangement comparable to the acyclic silyl derivatives. This result is expected because there is no significant release of angle strain in the six member ring upon formation of the intermediate shown below. The affect of ring strain on the rate of rearrangement (i.e. nucleophilic displacement) correlates with the available data on the affect of ring strain on the reactivity of tetravalent phosphorous to nucleophilic attack.[57,58]



Ring strain also affects the stereochemistry of nucleophilic displacement reactions on phosphorous.[3] Acyclic systems usually result in inversion, whereas a cyclic system, in which phosphorous is incorporated in a small ring usually results in retention of configuration. Displacement of a chlorine from silicon always results in inversion of configuration, except when the silicon is incorporated in a five member ring and retention of configuration is observed.[59] Incorporation of silicon into a six-member ring does not alter the stereochemical consequence of the reaction.[60,61]

Strictly analogous rearrangements are not known in carbon chemistry, however a similar degenerate migration of acetyl groups between two electronegative atoms has been reported.[62-64] An example is illustrated in reaction 21.[59] The reported activation

(21) 

energy is 15 kcal/mole.

F. Summary

The organosilyl β-diketonates studied all exhibit an open chain enol ether structure. In the ground state of these compounds the silicon atom is incipient pentacoordinate. Two factors are important in determining the degree of incipient pentacoordination: (1) The electron withdrawing or releasing abilities of the silyl and diketonate substituents and (2) The amount of angle strain at silicon.

The kinetic data for rearrangement of the cis isomer support a mechanism in which the bond making is an important step (i.e., the process is a nucleophilic displacement). The data also indicate the formation of a five coordinate intermediate. The increase in reactivity observed when the angle strain becomes large is due to a lowering of the energy of the intermediate relative to the ground state. The relative ΔG° values of the ground state of the cis isomer, calculated from the cis to trans ratios, differ by 1.3 kcal/mole when the ring size is decreased from six members to four members, whereas the $\Delta G^{\ddagger}$ values for rearrangement, differ by more than 6.4 kcal/mole. Pseudorotation about an equatorial oxygen atom as a pivot does not occur at any appreciable rate, but there is no evidence to exclude pseudorotation about an equatorial alkyl group as a pivot. In the absence of pseudorotation the displacement would require axial attack of the uncoordinated oxygen atom and equatorial departure of the leaving group. Although this does not violate the principle of microscopic reversibility,[65] it is chemically improbable since apical attack and departure should be the perferential modes of bond making and bond breaking. Apical bonds are longer and weaker than the equatorial bonds.[3] If one assumes apical attack and departure, then pseudorotation in the intermediate is required.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. M. Gielen, C. Dehouch, H. Mokhtar-Jamai, and J. Topart, Reviews on Silicon, Germanium, Tin and Lead Compounds, 1, 9 (1972).
2. L. H. Sommer, "Stereochemistry Mechanism and Silicon," McGraw-Hill Inc., New York, (1965).
3. K. Mislow, Accounts Chem. Res., 3, 321 (1970).
4. E. L. Muetterties, W. Mahler, and R. Schmutzler, Inorg. Chem., 2, 613 (1963).
5. J. J. Howe and T. J. Pinnavaia, J. Amer. Chem. Soc., 91, 5378 (1969).
6. T. J. Pinnavaia, W. T. Collins, and J. J. Howe, J. Amer. Chem. Soc., 92, 4544 (1970).
7. H. Shanan-Atidi and Y. Shvo, Tetrahedron Lett., 7, 603 (1971).
8. Y. N. Kuo, F. Chen, and C. Ainsworth, J. Chem. Soc. D, 137 (1971).
9. H. J. Reich and D. A. Murcia, J. Amer. Chem. Soc., 95, 3418 (1973).
10. D. A. O'Brien, and C. P. Hrung, J. Organomet. Chem., 27, 185 (1971).
11. N. Wiberg and H. J. Pracht, Chem. Ber., 105, 1388 (1972).
12. O. J. Scherer and P. Hernig, Chem. Ber., 101, 2533 (1968).
13. R. West and B. Bechlmeir, J. Amer. Chem. Soc., 94, 1649 (1972); and references therein.
14. M. Fukui, K. Itoh and Y. Ishii, J. Chem. Soc. PII, 1043 (1972).
15. J. Pump and E. G. Rochow, Chem. Ber., 97, 627 (1964).
16. J. F. Klebe, J. Amer. Chem. Soc., 90, 5246 (1968).
17. J. F. Klebe, Accounts Chem. Res., 3, 299 (1970).
18. F. P. Boer and F. P. Van Remoorten, J. Amer. Chem. Soc., 92, 801 (1970).
19. H. P. Fritz and C. G. Kreiter, J. Organomet. Chem., 4, 313 (1965).

20. A. Davison and P. E. Rakita, Inorg. Chem., 9, 289 (1970).

21. A. J. Ashe, Tetrahedron Lett., 24, 2105 (1970).

22. H. Kwart and J. Slutsky, J. Amer. Chem. Soc., 94, 2515 (1972).

23. H. M. Frey and R. Walsh, Chem. Rev., 69, 103 (1969).

24. T. K. Kusnezowa, K. Ruhlmann, and E. Grundemann, J. Organomet. Chem., 47, 53 (1973).

25. A. G. Brook, D. M. MacRae, W. W. Limburg, J. Amer. Chem. Soc., 89, 5494 (1967).

26. A. G. Brook and J. D. Pascoe, J. Amer. Chem. Soc., 93, 6224 (1971).

27. Ward T. Collins, M.S. Thesis, Michigan State University (1970).

28. R. Damrauer, R. A. Davis, M. T. Burke, R. A. Karn, and G. T. Goodman, J. Organomet. Chem., 43, 121 (1972).

29. R. West, J. Amer. Chem. Soc., 76, 6012 (1954).

30. W. A. Krines, J. Organomet. Chem., 29, 1601 (1964).

31. C. L. Frye, J. M. Klosowski, and D. R. Weyenberg, J. Amer. Chem. Soc., 92, 6379 (1970).

32. C. L. Frye, J. M. Klosowski, J. Amer. Chem. Soc., 94, 7186 (1970).

33. V. M. Vdovin, N. S. Nametkin, and P. L. Grinberg, Dokl. Akad. Nauk SSSR., 150, 799 (1963).

34. R. West, J. Amer. Chem. Soc., 80, 3246 (1958).

35. K. A. Andrianov and L. M. Khananashvili, Organomet. Chem. Rev., 2, 141 (1967).

36. R. T. Conley, "Infrared Spectroscopy, Allyn and Bacon Inc., Boston (1972).

37. J. J. Howe, Ph.D. Thesis, Michigan State University, East Lansing, Michigan, 1971.

38. R. Damrauer, Organomet. Chem. Rev. A, 8, 67 (1972).

39. E. Akerman, Acta. Chem. Scand., 11, 373 (1957).

40. R. C. Mehrotra, International Symposium on Organosilicon Chemistry, Prague, 1965.

41. L. V. Vilkov, V. S. Mastryukov, Y. V. Vaurova, V. M. Udoven, and P. L. Grinberg, *Dokl. Akad. Nauk SSSR*, *177*, 1508 (1967).

42. J. Laane and R. C. Lord, *J. Chem. Phys.*, *48*, 1508 (1968).

43. K. G. Dzhaparidze, Canadidates Thesis, Moscow, 1955, see ref. 35.

44. W. H. Knoth, Ph.D. Thesis, the Pennsylvania State University, University Park, Pennsylvania 1954.

45. A. G. Brook, M. A. Zuigley, G. J. D. Peddle, N. V. Schwartz and C. M. Warner, *J. Amer. Chem. Soc.*, *82*, 5102 (1960).

46. A. G. Brook and J. B. Pierce, *Can. J. Chem.*, *42*, 298 (1964).

47. Private communication, Alan Schwartz, Michigan State University, East Lansing, Michigan.

48. J. Frye, Ph.D. Thesis, Michigan State University, East Lansing, Michigan.

49. E. D. Bailer, M.S. Thesis, Michigan State University, East Lansing, Michigan, 1969.

50. H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, *25*, 1228 (1956).

51. D. Kost, E. A. Carlsen, and M. Raban, *Chem. Commun.*, 656 (1971).

52. T. J. Pinnavaia, J. M. Sebeson, II, and D. Case, *Inorg. Chem.*, *8*, 644 (1969).

53. F. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, *88*, 2951 (1966).

54. L. A. Sommer, O. F. Bennett, P. G. Campbell, and D. R. Weyenberg, *J. Amer. Chem. Soc.*, *79*, 3295 (1957).

55. L. H. Sommer and O. F. Bennett, *J. Amer. Chem. Soc.*, *79*, 1008 (1957).

56. L. H. Sommer, W. P. Baree, Jr., and D. R. Weyenberg, *J. Amer. Chem. Soc.*, *81*, 251 (1959).

57. F. H. Westheimer, *Accounts, Chem. Res.*, *1*, 70 (1968).

58. R. F. Hudson and C. Brown, *Accounts Chem. Res.*, *5*, 204 (1972).

59. D. N. Roark, L. H. Sommer, *J. Amer. Chem. Soc.*, *95*, 969 (1973).

60. R. Corriee and J. Masse, *Bull. Soc. Chim. Fr.*, 3491 (1969).

61. H. Sakurai and Murakami, *J. Amer. Chem. Soc.*, *94*, 5081 (1972).

62. V. I. Minkin, L. P. Olekhnovich, Yu. A. Zhdanov, V. V. Kislev, M. A. Voronev, L. E. Nivorozhkin and Z. N. Budarina, *Dokl, Akad. Nauk SSSR*, *204*, 1363 (1972).

63. I. C. Calder, D. W. Cameron, and M. D. Sidell, *Chem. Commun.*, 360 (1971).

64. J. Castells, M. A. Merino, and M. Morino-Manas, *Chem. Commun.*, 709 (1972).

65. R. L. Burwell, Jr., and R. G. Pearson, *J. Phys. Chem.*, *70*, 300 (1966).

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