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SOLVENT-CATALYZED *cis—trans* ISOMERIZATION OF HALOSILACYCLO-BUTANES AND -PENTANES. EVIDENCE FOR CATIONIC INTERMEDIATES WITH EXPANDED COORDINATION

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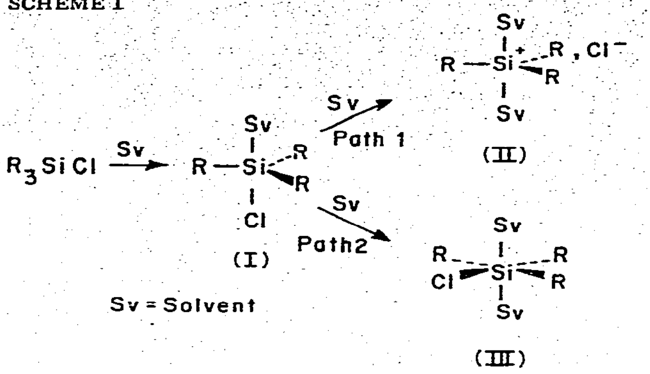
Summary

1-Chloro-1,2,-dimethylsilacyclo-butane (IV) and-pentane (V) undergo *cis—trans* isomerization catalyzed by a variety of nucleophilic species, including polar aprotic solvents. Kinetics of the process have been investigated for HMPT in CCl_4. Rate laws and the observation of HMPT-catalyzed halogen exchange between bromo- and chloro-silanes lead to the conclusion that 5-coordinate siliconium ions are intermediates in this process. Evidence is also presented that pentacoordinate species formed from V (but not from IV) undergo rapid pseudorotations.

Halosilanes are the basic building materials for organosilicon compounds, serving principally as substrates for displacement reactions taking place at Si. Hence it is of considerable interest to define the interactions, including reaction pathways, of halosilanes with nucleophilic species. The racemization of chlorosilanes with solvents of high dielectric constant is such an interaction. The racemization was first suggested by Sommer to involve ionization to a silyl cation [1]. However, the process has been extensively studied recently by Corriu and coworkers [2] who have shown a marked decrease in rates of racemization with increasing steric size of substituents. The reverse order of reactivity would be predicted for ionization to an sp^2 silyl cation. Also the racemization with dimethylformamide (DMF), dimethylsulfoxide (DMSO), and hexamethylphosphorus triamide (HMPT) has been demonstrated to be first-order in chlorosilane and second-order in solvent [3] and the order of reactivity of the various halogens has been found to be SiF < SiCl < SiBr [4].

On these bases Corriu proposed two possible mechanisms, both involving an initial coordination of one solvent (Sv) molecule to silicon to form a pentacoordinate intermediate (I) (Scheme 1) followed by addition of a second solvent molecule to either displace chloride ion (Path 1) or form a hexacoordinate

SCHEME 1



species (Path 2). Precedent exists for formation of both pentacoordinate siliconium ions [5] and hexacoordinate species [6] as stable entities, although particularly with respect to the latter, a number of highly electronegative substituents seem to be required to confer stability. Either pathway would result in racemization since both II and III are symmetrical. A study of substituent effects failed to differentiate the two mechanisms [4].

In an effort to decide which mechanism is operating we have studied the kinetics of isomerization of 1-chloro-1,2-dimethylsilacyclobutane (IV) and 1-chloro-1,2-dimethylsilacyclopentane (V). If II is the intermediate through which racemization occurs, IV and, to a lesser extent, V might be expected to show decreased rates of isomerization relative to acyclic or large ring chlorosilanes since the C—Si—C angle in II is ca. 120° but in IV is ca. 80° [7] and in V ca. 96° [8]. Conversely, if III is the intermediate in racemization, IV and V should show greater rates of isomerization since the C—Si—C angle in III (ca. 90°) is close to that present in IV and V.

Further, we believed that if silicon—halogen bond-breaking occurs halide—halide exchange could possibly be observed. We have reported preliminary data concerning the isomerization of IV [9], and we now report fully on the kinetics and exchange reactions observed with IV and with V.

TABLE 1

PSEUDO-FIRST-ORDER RATE CONSTANTS IN CCl_4 AT 45 ± 1°C

10^5 [HMPT] (M)	$10^6 k_1$ (sec^{-1})	
	E-IV [a]	E-V [b]
500		825 ± 40
300		280 ± 10
200	3600 ± 300	129 ± 6
100	1600 ± 100	
50	800 ± 30	17 ± 2
25	310 ± 20	6.2 ± 0.2
10	112 ± 6	1.7 ± 0.2
5.0	43 ± 2	
2.5	15 ± 1	

[a] 0.75 M in IV. [b] 0.90 M in V.

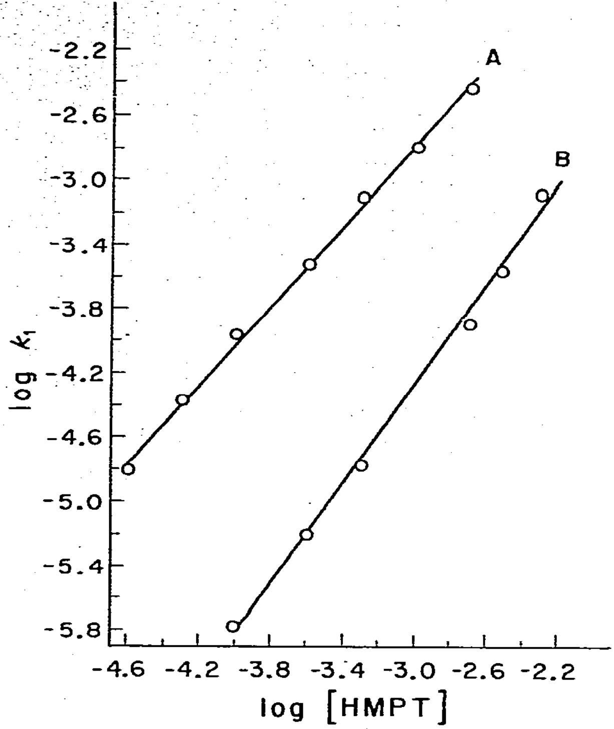


Fig. 1. Log k_1 vs. log [HMPT] for isomerization of IV (A) and V (B) in CCl_4 at 45°C.

Results

We and others have previously reported the preparations of the 1,2-dimethylsilacyclo-butane [10] and -pentane [11] ring systems and means for obtaining mixtures of geometric isomers enriched in *E* and/or *Z* component. The chlorosilanes, IV and V, undergo isomerization catalyzed by a variety of polar, aprotic species. These include HMPT, nitromethane, tetrahydrofuran, sulfolane, pyridine and quinoline. DMF and DMSO not only gave isomerization but also re-

TABLE 2

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR ISOMERIZATION OF IV IN CCl_4 AT 45 ± 1°C

10^4 [HMPT] (*M*)	[IV] (*M*)	10^4 k_1 (sec^{-1})
10	0.75	16 ± 1
10	0.30	14 ± 2
5.0	1.13	9.7 ± 0.8
5.0	0.75	8.0 ± 0.3
5.0	0.30	6.6 ± 0.7
2.5	0.75	3.1 ± 0.2
2.5	0.30	2.6 ± 0.2
1.0	0.75	1.12 ± 0.06
1.0	0.30	1.14 ± 0.05

TABLE 3

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR ISOMERIZATION OF IV AND V BY HMPT IN CCl_4

Temperature (°C)	$10^5\,k_1$ for IV[a] (sec^{-1})	$10^4\,k_1$ for V[b] (sec^{-1})
56	88 ± 7	
55		13.3 ± 0.5
50		11.6 ± 0.5
45	70 ± 6	9.6 ± 0.4
40		7.7 ± 0.4
35	37 ± 2	7.6 ± 0.5
24	20 ± 1	
23		5.1 ± 0.2
14		3.3 ± 0.2
11	7.1 ± 0.5	
4		2.3 ± 0.2
—2	2.5 ± 0.1	

Compound	E_a (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)
IV	11 ± 1	10.5 ± 1	—41 ± 2
V	6.2 ± 0.1	5.5 ± 0.1	—55 ± 1

[a] 0.75 *M* in IV. [b] 0.90 *M* in V.

acted with IV and V at a rate comparable to that of isomerization. The nature of the products in the latter reactions has not been determined in our work, but they are probably siloxanes as has been previously observed in reactions of DMSO and DMF with chlorosilanes [12].

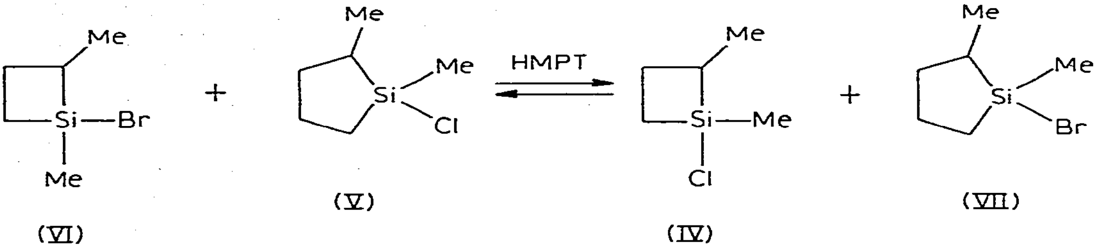
The isomerization of an 85 : 15 mixture of *E*-IV and *Z*-IV, respectively and of a 90 : 10 mixture of *E*-V and *Z*-V were followed by observation of the Si—Me region of the NMR spectrum. The isomerization of both IV and V showed good pseudo-first-order kinetics. The pseudo-first-order rate constants k_1 obtained at various HMPT concentrations are shown in Table 1. Plots of log k_1 vs. [HMPT] (Fig. 1) gave good straight lines from which were calculated apparent orders in HMPT of 1.23 ± 0.05 and 1.6 ± 0.1 for IV and V, respectively.

Table 2 gives the pseudo-first-order rate constants observed at various concentrations of IV. Since the method used in following the isomerization limited the range of possible chlorosilane concentrations, k_1 was determined for only three concentrations of IV but was checked at various HMPT concentrations. The results show that although the rate increased slightly with increasing concentrations of IV, the difference was insufficient to warrant the inclusion of chlorosilane concentration in the pseudo-first-order rate constant. It seemed most reasonable to attribute the small rate increase to a change in solvent polarity due to increasing chlorosilane concentration. Activation parameters for the isomerization of IV and V, and the data from which they were obtained, are presented in Table 3. The results are comparable to the values reported by Corriu [3].

In order to determine if halide—halide exchange occurs, 1-bromo-1,2-dimethyl-1-silacyclobutane (VI) and V were added in a 1 : 1 ratio to CCl_4 which was ca.

$1 \times 10^{-2}\ M$ in HMPT (Scheme 2). Rapid formation of IV and 1-bromo-1,2-dimethyl-1-silacyclopentane (VII) occurred, equilibrium being attained in less than 10 minutes. In the absence of HMPT little exchange occurred even after 5 days. The development of quantitative rate data in this quite complicated system was not attempted, but rates of isomerization and exchange could be observed to be comparable.

SCHEME 2



Similarly, halide—halide exchange induced by HMPT was observed in the following mixtures: trimethylchlorosilane and VI; diphenylmethylbromosilane (VIII) and IV; V and VIII; and trimethylchlorosilane and VIII. A similar fluoride—chloride exchange catalyzed by amines and Ph_3P has previously been reported [13a] *.

Discussion

The observed fractional orders in HMPT for isomerization of IV and V suggest that the observed rate, k_1, is the sum of a first-order reaction and a second-order reaction in HMPT (eq. 1). The rate data for isomerization of V fit this expression

$$k_1 = k_a[\mathrm{HMPT}] + k_b[\mathrm{HMPT}]^2 \qquad (1)$$

with $k_a = 1.4 \times 10^{-2}\ M^{-1}\ \mathrm{sec}^{-1}$ and $k_b = 28.8\ M^{-2}\ \mathrm{sec}^{-1}$, as determined from the graph of $k_1/[\mathrm{HMPT}]$ vs. [HMPT] (Fig. 2). However, the corresponding graph for the isomerization of IV (Fig. 3) is nonlinear. Inspection of Fig. 3 reveals that at high HMPT concentrations ($>5 \times 10^{-4}\ M$) the isomerization is first-order in HMPT (slope = 0) but at lower HMPT concentrations the isomerization is second-order in HMPT. These kinetic observations are consistent with two-step formation of an intermediate (Scheme 3) in which the rate-determining step changes with changing HMPT concentration.

SCHEME 3

$$\mathrm{Sv} + \mathrm{R_3SiCl} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{R_3SiCl(Sv)} \xrightarrow[\mathrm{Sv}]{k_5} \mathrm{R_3SiCl(Sv)_2}$$

(XI)

Application of the steady-state assumption to the adduct containing one Sv yields the kinetic law of eq. 2, and the observed rate constant, k_1, is therefore

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* A similar Si—F/Si—Cl exchange catalyzed by relatively large amounts of HMPT has recently been observed [13b].

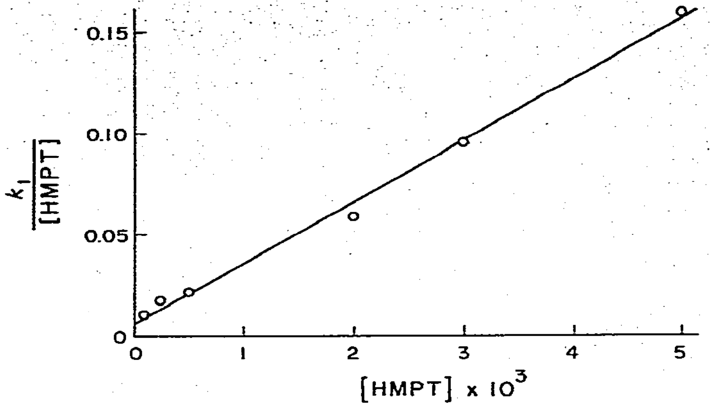


Fig. 2. k_1/[HMPT] vs. [HMPT] for isomerization of 1-chloro-1,2-dimethylsilacyclopentane (V) in CCl_4 at 45° C.

defined as in eq. 3. The line shown in Fig. 3 is a plot of eq. 3 with $k_4 = 1.7\ M^{-1}$ sec^{-1} and $k_5/k_{-4} = 2 \times 10^4\ M^{-1}$.

$$\text{rate} = \frac{k_4 k_5 [\text{Sv}]^2 [\text{R}_3\text{SiCl}]}{k_{-4} + k_5 [\text{Sv}]} \tag{2}$$

$$k_1 = \frac{k_4 k_5 [\text{Sv}]^2}{k_{-4} + k_5 [\text{Sv}]} \tag{3}$$

The same kinetic scheme was used by Schowen, Swain, and co-workers to explain kinetic data they obtained for hydrolysis of *p*-methoxyphenoxytriphenylsilane [14]. However, Eaborn and co-workers have recently challenged Schowen's data, suggesting the solvent used by Schowen's group contained an acidic impurity [15]. Such an explanation does not appear likely for the data obtained with IV since different results were obtained with V using the same solvents and com-

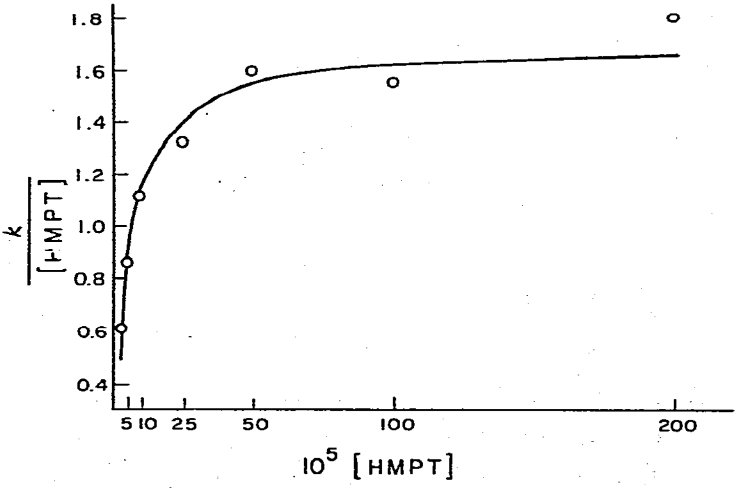


Fig. 3. k_1/[HMPT] vs. [HMPT] for isomerization of 1-chloro-1,2-dimethylsilacyclobutane (IV) in CCl_4 at 45°C.

parable concentrations. Also in contrast to the previous investigations, we are presently dealing with a system which is clearly second order in nucleophile under a variety of conditions employing both Si [3,16] and Sn [17] atoms as the metalloid center undergoing stereomutation. A similar kinetic scheme is being proposed for those processes, with the simple exception that $k_{-4} >> k_5$.

At low concentrations of HMPT ($<10^{-5}$ M), the term k_5 [Sv] in eq. 3 becomes small relative to k_{-4} and, therefore, negligible. The observed rate constant k_1 is then defined as eq. 4 and a third order rate constant k_3 can be introduced (eq. 5).

$$k_1 = \frac{k_4 k_5 [\mathrm{Sv}]^2}{k_{-4}} \tag{4}$$

$$k_3 = \frac{k_1}{[\mathrm{Sv}]^2} = \frac{k_4 k_5}{k_{-4}} = 3.4 \times 10^4\ M^{-2}\ \mathrm{sec}^{-1} \tag{5}$$

This is in good agreement with $k_1/[\mathrm{Sv}]^2 = 2.4 \times 10^4$ M^{-2} sec^{-1} for the reaction at 2.5×10^{-5} M in HMPT where it is approaching second-order in HMPT. Comparison of k_3 with the third-order rate constant reported by Corriu for the racemization of i-PrPhNpSiCl (IX) with HMPT [3] ($k_3 = 4 \times 10^{-2}$ M^{-2} sec^{-1}) revealed that IV reacted ca. 5×10^5 times faster. A comparable value for the isomerization of V is k_b from the term which is second order in HMPT (see eq. 1). The four-membered ring, IV, isomerizes ca. 8×10^2 times faster than the five-membered ring, V, which isomerizes ca. 7×10^2 times faster than the acyclic example, IX. Since EtPhNpSiCl (X) racemizes ca. 36 times faster than the isopropyl derivative IX [3], some steric factors are clearly involved in determining the relative reactivities in these processes. It would appear difficult to make a case that the silacyclopentane (V) is showing an acceleration due to ring strain and not just due to steric factors. However, the more rapidly isomerized silacyclobutane (IV) does appear to be getting some assistance from other than steric affects, presumably from ring strain. Acceleration in the formation of extracoordinate intermediates is frequently ascribed to ring strain factors in organophosphorus displacement reactions [18a,19], and the same suggestion has been made for organosilicon reactions [18b]. Acceleration in the isomerization of IV is thus not suprising, but there is a surprising feature to the results; namely that k_5 (Scheme 2) is not clearly rate-determining in isomerization of IV, whereas the corresponding step is rate-determining in acyclic systems. Thus with the silacyclobutane the second step is being accelerated even more than the initial formation of a pentacoordinate intermediate.

Because it is well known that rapid exchange occurs between halosilanes and inorganic halide [1,20—22], the rapid halogen—halogen exchange observed in Scheme 2 suggests that the isomerization of IV and at least the third order portion of the isomerization of V are proceeding through ionic intermediates:

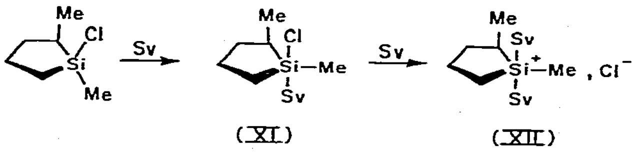
$$R_3Si(Sv)_2^+, X^- + R'_3SiX' \rightarrow R_3Si(Sv)_2^+, X'^- + R'_3SiX$$

This reaction must be fast relative to formation of the intermediates and it presumably goes with retention of configuration; otherwise the kinetics for isomerization would be more complex. There are cases in which halide—halide exchange with halosilane occurs with inversion [21,23], however retention is a more reasonable assumption since chloride—chloride exchange in benzene (a solvent similar in polarity to CCl_4) has been shown to proceed with almost complete retention [22], and strained rings should show a bias toward retention [10,19,24].

That the solvent adduct formed from IV and V with HMPT should be ionic is a reasonable assumption also. Numerous solvent adducts are known for halosilanes with DMF, DMSO, acetonitrile, trimethylphosphine oxide and amines [25]. The organic base adducts of bromo- and iodo-silanes are clearly ionic from conductivity and infrared measurements [26,27], and data for chlorosilanes are indicative of ionic structures also [27]. We believe our proposals thus far are quite logically consistent. Nevertheless, it is possible to propose that the isomerization and exchange reactions are occurring through unrelated mechanistic pathways. We are convinced by the substantially identical rates for the two processes that it is much more reasonable to propose a single mechanism.

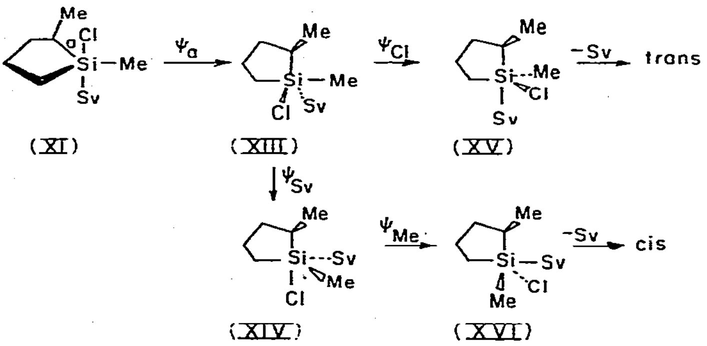
Specific forms for the intermediates that are in agreement with previous proposals can be assigned for the isomerization of V. We propose Scheme 4 to account for the third order component of the isomerization of V, which is in complete accord with Path 1 in Scheme 1 proposed by Corriu for isomerization of acyclic halosilanes. Intermediate XI, although having both ring bonds equatorial, is the most logical first intermediate to propose, since we have shown in earlier work [11a] that displacements of good leading groups from Si in the silacyclopentane system proceed with inversion, as with acyclic silanes. The retention proposed for conversion of XI to XII has no known analogy in Group IV, however Martin has recently shown that displacement of an axial group in a sulfurane proceeds with retention [28]. The intermediate XII can then be a precursor of either *cis*- or *trans*-chloride when it returns to starting material.

SCHEME 4



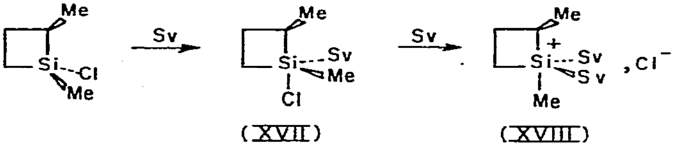
We propose that the minor second order component to the isomerization of V is proceeding by way of pseudorotations of the initial five-coordinate intermediate (Scheme 5). The most stable forms of the intermediate are presumably those like XIV—XVI which have one of the electronegative substituents (Cl or Sv) axial and one of the ring bonds axial, although it could reasonably be argued that since all of the intermediates have some drawbacks, they are likely to be closer in energy than those which one can draw for silacyclobutane or acyclic systems. A reasonable consequence of having the intermediates close together in energy would be their ready interconversion, and consequently one would be more likely to see pseudorotations in the silacyclopentane system. A single Berry pseudorotation of XI will not give one of the presumably most stable intermediates, but will give an intermediate like XIII. Pseudorotation of XIII could place either Sv or Cl axial as in XV or XIV, respectively. The latter two pseudorotation processes are likely to be competitive, and XV can lead directly to one isomer, while the shortest route from XIV will lead to the other isomer.

SCHEME 5



A complete accounting for the isomerization of IV is not so straightforward. Previous work [10] indicates that it is not reasonable to expect the silacyclobutane ring to span two equatorial positions in an intermediate trigonal bipyramid. Scheme 6 presents a reasonable possibility. The pseudosymmetric intermediate, XVIII, is the most economical one to propose on a route from *cis*-IV to *trans*-IV, although it would not be expected to be the most stable possible intermediate. XVIII would be formed from XVII by attack of Sv on a trigonal bipyramidal edge. XVII could be formed either directly by equatorial attack of Sv, for which there is precedent in Si chemistry [29], or by axial attack of Sv followed by a single pseudorotation. As an alternative to Scheme 6 it is possible to propose that extensive pseudorotations of five coordinate siliconium ions occur, however no direct evidence exists to indicate that such extensive stereomutations occur in extracoordinate intermediates formed from silacyclobutanes, although evidence for the stereomutation has been sought [30].

SCHEME 6



Experimental

General

Carbon tetrachloride (reagent grade) was supplied by Mallinckrodt Chemical Works and dried over 4 Å molecular sieves prior to use. Hexamethylphosphoric triamide (HMPT) was dried over CaH_2 prior to distillation. A 1.0×10^{-2} *M* stock solution of HMPT in CCl_4 was prepared by diluting 174 μl (0.1792 g, 1.00 mmol) of HMPT to 100 ml. All other solutions were prepared by successive dilution of the stock solution. Although the kinetic data for isomerization of IV and V were collected by two different workers the same solutions of HMPT in CCl_4 were used by both. The 85 : 15 mixture of *E*-IV and *Z*-IV and the 90 : 10 mixture of *E*-V and *Z*-V were prepared by the methods previously described [10d,11a]. The preparations of diphenylmethylchlorosilane [31] and diphenylmethylbromosilane [32] were carried out according to published procedures.

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian A60A, equipped with a V-4343 variable temperature controller. The temperature of the cavity of the NMR was determined by the difference in chemical shifts of an ethylene glycol sample or a methanol sample. All glassware was dried in an oven at 160°C for at least two hours and cooled in a desiccator over $CaSO_4$.

Kinetic measurements

In all cases the reaction was followed by NMR. The standard procedure was to place in a dry NMR tube via syringe 0.50 ml of a solution of known concentration of silyl chloride in CCl_4. The tube was placed in the cavity of the spectrometer held at 45 ± 1°C. After allowing ca. 5 minutes for the temperature to equilibrate, 0.50 ml of a solution of known concentration of HMPT in CCl_4 was added via syringe. At definite time intervals the Si—Me region (δ 0.35 to 0.60 ppm) was integrated on a 100 Hz sweep width to obtain the ratio of *E*-isomer to *Z*-isomer. The reaction was followed until the approximate equilibrium ratio of *E*-isomer to *Z*-isomer was obtained or until at least 35 points were taken. The equilibrium constant (K_{eq}) for the isomerization of silyl chloride by HMPT was determined by allowing three different runs to proceed for at least 10 half-lives and then repeatedly integrating the sample. From an average of the 18 integrations made, the equilibrium constant was determined to be 1.08 for IV and 1.16 for V. The pseudo-first-order rate constants, k_1, were obtained from a plot of the standard equation describing approach to equilibrium [33] which yields the sum of forward and reverse rate constants, from which k_1 was derived through knowledge of K_{eq}. Activation parameters were determined in the usual manner from a plot of log k_1 vs. $1/T$.

Treatment of data

All points in which the sum of the integrations of the *E* and *Z* isomers deviated greater than 1.96 times the standard deviation (σ) (95% confidence level) were discarded. Similarly, all points if any that deviated greater than 1.96 times the standard error of estimate ($S_{y,x}$), as determined by a regression analysis, were disregarded. A second regression analysis thus provided the slope (95% confidence level).

Isomerization of E-IV and E-V with various solvents

In general the isomerization of IV and V with various solvents was carried out by adding ca. 0.1 ml of the solvent to 1 ml of an 85 : 15 mixture of *E*-IV and *Z*-IV or a 90 : 10 mixture of *E*-V and *Z*-V in CCl_4 and observing any change in the ratio by NMR at ambient temperature. With IV, pyridine, quinoline, DMSO, DMF, and HMPT gave complete isomerization in <1 h. Sulfolane and nitromethane required ca. 24 h while acetonitrile gave no isomerization after 18 h. THF and acetone gave no isomerization of silyl chloride at room temperature, but when a sample of silyl chloride containing a trace of either THF or acetone was held at 115°C for 2 h isomerization was complete. With V, pyridine and DMSO showed complete isomerization in <10 min, while sulfolane required 48 h. Complete isomerization by THF required ca. 8 h at 60°C.

Halide—halide exchange catalyzed by HMPT

In a 25 ml flask equipped with a magnetic stirrer and set for distillation were placed 1.95 g (10.9 mmol) of VI, 2.4 g (21.8 mmol) of trimethylchlorosilane, and 10 ml of 2×10^{-4} *M* HMPT in CCl_4. After stirring 2 h at room temperature, the mixture contained a ca. 60 : 40 mixture of VI and IV respectively as determined by NMR. Distillation gave a fraction, b.p. 60—68°C/95 mmHg, the mass spectrum and NMR of which were identical to those of IV.

In general the halide—halide exchange of chloro- and bromo-silanes in the presence of HMPT was determined by dissolving equivalent amounts (ca. 0.1 g) of the appropriate bromo- and chloro-silane in 0.5 ml of a 1×10^{-2} *M* HMPT in CCl_4 solution. The exchange was followed by observing the Si—Me region (δ 0.35 to 0.7 ppm) of the NMR spectrum and comparing the chemical shifts observed with those obtained for the previously isolated pure compounds. Halide—halide exchange induced by HMPT was observed in the following mixtures: 1-chloro-1,2-dimethylsilacyclopentane (V) and 1-bromo-1,2-dimethylsilacyclobutane (VI); bromodiphenylmethylsilane (VIII) and IV; VIII and V; and trimethylchlorosilane and VIII. In the absence of HMPT, no exchange was noted for the previously described mixtures in CCl_4.

Acknowledgements

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