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STEREOCHEMISTRY OF REACTIONS IN THE 1,2-DIMETHYLSILACYCLOPENTANE RING SYSTEM. II. STEREOSELECTIVE TRANSFORMATION*

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SUMMARY

A number of stereoselective reactions of 1-substituted-1,2-dimethylsilacyclopentanes are described. Reactions of the silyl chloride (II) with ZnF_2 and with alcohols catalyzed by amines are stereoselective as a result of rapid isomerization of II. Alcoholysis of silicon hydride (I) catalyzed by transition metals is apparently an inversion reaction regardless of the nature of the catalyst, but can appear to be stereoselective because of isomerization of alkoxysilane product. Reduction of silyl fluoride (IV) by lithium aluminum hydride is nonstereoselective, a result which is proposed to arise through rapid isomerization of intermediates with expanded coordination.

INTRODUCTION

In the preceding paper in this series [4] we have reported preparation of numerous 1-substituted 1,2-dimethylsilacyclopentanes and have demonstrated that they undergo a number of stereospecific transformations, behaving therein more like acyclic silanes than like the 1,2-dimethylsilacyclobutanes previously

*Preliminary communications of portions of this work have appeared. (Refs. 1-3)

investigated in our laboratories [5-8]. We have discussed the role of ring strain in contributing to this behavior. We now wish to report a number of stereoselective reactions of the silacyclopentanes demonstrating in some cases completely different behavior from either less-strained acyclics or more-strained cyclics, and including good evidence that extracoordinate intermediates are formed and that they can undergo pseudorotations at observable rates.

The assignments of Z and E configurations necessary for the stereochemical studies have been discussed in detail in the first part of this work [4] and in the references cited therein. The assignments are based mainly on NMR chemical shifts. Table 1 contains the principal NMR absorptions used for structural assignments for the new compounds reported in this paper.

TABLE 1. NMR SPECTRA OF 1-SUBSTITUTED 1,2-DIMETHYLSILACYCLOPENTANES*

Compound	δ $^{1}H(Si-CH_3)$	δ $^{1}H(C_2-CH_3)$	δ $^{13}C(Si-CH_3)$
E-$SiOCH_3$ (VII)	0.11	1.05	-5.3
Z-$SiOCH_3$ (VII)	0.15	1.10	-3.2
E-$SiOCH_2CH_3$ (VIII)	0.11		
Z-$SiOCH_2CH_3$ (VIII)	0.14		
E-$SiOCH(CH_3)_2$ (IX)	0.11		
Z-$SiOCH(CH_3)_2$ (IX)	0.15		
E-$SiOC(CH_3)_3$ (X)	0.11		
Z-$SiOC(CH_3)_3$ (X)	0.15		
E-$SiOC_6H_{11}$-cyclo (XI)	0.11		
Z-$SiOC_6H_{11}$-cyclo (XI)	0.14		
E-$SiN(CH_3)_2$ (XII)	0.05		
Z-$SiN(CH_3)_2$ (XII)	0.11		
E-$SiN(C_2H_5)_2$ (XIII)	0.05		
Z-$SiN(C_2H_5)_2$ (XIII)	0.10		

*Chemical shifts measured in ppm downfield from TMS as internal standard. Complete spectra are presented in the experimental section.

RESULTS AND DISCUSSION

The stereochemical results of a number of reactions of 1-substituted 1,2-dimethylsilacyclopentanes are listed in Tables 2-4. Most of these reactions are

stereoselective, but the stereoselectivity does not always arise in the same step in the mechanism, hence the different types will be discussed separately. In several of the reactions noted in Table 2, the stereoselectivity arises, at least in part, from isomerization of 1-chloro-1,2-dimethylsilacyclopentane (II) prior to reaction. We have already noted [5,7,8] a propensity toward facile isomerization on the part of the corresponding chlorosilacyclobutane, and the same can be said, to a somewhat lesser degree [8] about II. Perhaps the simplest example of stereoselectivity noted in Table 2 is the case of zinc fluoride reaction with II. In that case, following the reaction by ^{1}H NMR, II is isomerized at a rate much faster than reaction, and the mixture of silylfluoride isomers produced is essentially the same as the equilibrium mixture of chloride isomers (50/50). The equilibration of II has been followed also under somewhat different conditions [8], as has that of Si-F (IV, see below), and both have equilibrium mixtures that are approximately 50/50 in the two isomers.

TABLE 2. STEREOCHEMISTRY OF SOME REACTIONS OF 1-HALOSILACYCLOPENTANES

Compound	Z/E	Reagent	Product	Z/E
SiCl (II)	80/20	ZnF_2	SiF (IV)	54/46
SiCl (II)	55/45	ZnF_2	SiF (IV)	54/46
SiCl (II)	55/45	p-$MeOC_6H_4MgBr$	SiC_6H_4OMe-p (VI)	7/93*
SiCl (II)	86/14	p-$MeOC_6H_4MgBr$	SiC_6H_4OMe-p (VI)	10/90
SiCl (II)	50/50	$(CH_3)_2NH$	$SiN(CH_3)_2$ (XII)	35/65
SiCl (II)	50/50	$(C_2H_5)_2NH$	$SiN(C_2H_5)_2$ (XII)	30/70
SiF (IV)	5/95	$LiAlH_4$	SiH (I)	44/56
SiF (IV)	30/70	$LiAlH_4$	SiH (I)	47/53
SiF (IV)	50/50	$LiAlH_4$	SiH (I)	45/55
SiF (IV)	77/23	$LiAlH_4$	SiH (I)	49/51
SiCl (II)	50/50	cyclo-$C_6H_{11}OH$/ quinoline	$SiOC_6H_{11}$-cyclo (XI)	7/93
SiCl (II)	50/50	$(CH_3)_3COH$/quinoline	$SiOC(CH_3)_3$ (X)	3/97

* For experimental see preceding paper [4].

Rather more interesting, and obviously more complex is the alcoholysis of II catalyzed by amines (Table 3 and last two entries in Table 2), in which the composition of the product mixture is a function of the nature of the amine catalyst as well as of the alcohol. The amine-catalyzed alcoholysis reaction has been much discussed in terms of mechanism [9,10], but no work has clearly

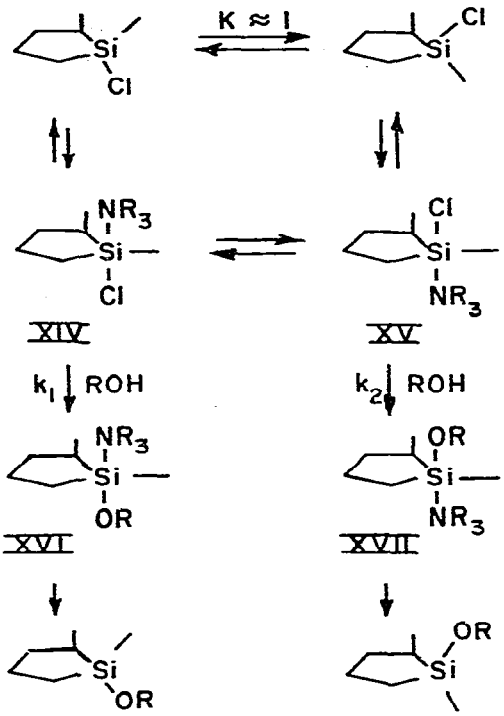
TABLE 3. PRODUCT RATIOS IN AMINE-CATALYZED ALCOHOLYSIS OF 1-CHLORO-1,2-DIMETHYLSILACYCLOPENTANE (Z/E = 50/50) BY METHANOL, ETHANOL, AND 2-PROPANOL

Amine	Product Ratio $SiOCH_3$ (VII) Z/E	$SiOCH_2CH_3$ (VIII) Z/E	$SiOCH(CH_3)_2$ (IX) Z/E
Aniline	60/40	40/60	37/63
N-Methylaniline	30/70	30/70	12/88
Pyridine	52/48	40/60	14/86
Quinoline	35/65	30/70	10/90
Cyclohexylamine	30/70	25/75	10/90
Triethylamine	33/67	35/65	10/90
Isopropylamine	55/45	30/70	12/88

defined the role of the amine. It obviously does complex the HCl formed in the alcoholysis and thereby affects the equilibrium position in the system. It apparently is involved kinetically as a catalyst [11], but the kinetic effect is not always seen [12]. There is catalysis by HCl produced in the reaction and by added ammonium chloride [13-15], and both are acting as general base catalysts coordinated with the alcohol proton, HCl being present in largely undissociated form in inert solvents and ammonium chlorides presumably present as ion pairs [13]. Added amine can presumably either act as a general base catalyst itself, or as reaction proceeds it could be converted to ammonium chloride which acts as catalyst.

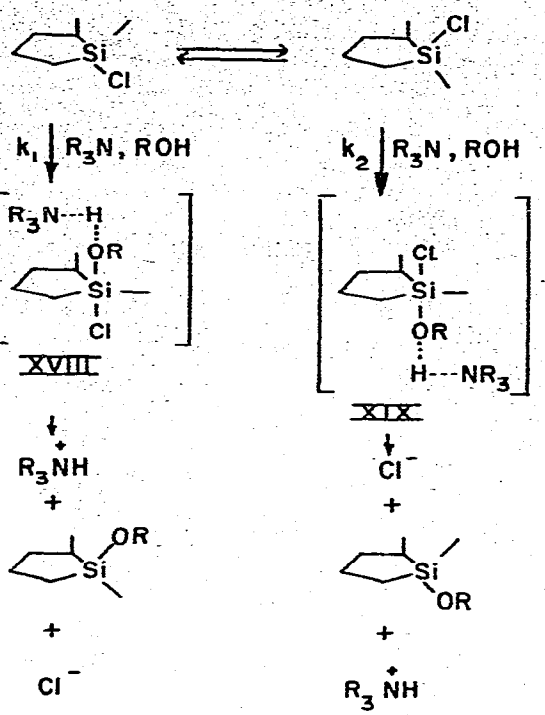
The present results indicate that in methanolysis in particular the nature of the amine plays a major role in determining product composition. However, amine can be shown to act in another capacity as well in interactions with halosilanes. It has been shown that chlorosilanes undergo racemization or isomerization reactions with donor molecules by way of a mechanism involving expanded coordination [8,16]. Pyridine and quinoline are among the reagents that give rise to rapid isomerization of 1-chloro-1,2-dimethylsilacyclobutane and II. It is thus reasonable to propose that stereoselectivity in the alcoholysis of II arises due to the rapid equilibrium established between Z-II and E-II ($K \approx 1$) by way of species with expanded coordination such as XIV and XV in Scheme I (which are not, however, the only intermediates involved.)

Scheme I



The stereoselectivity does not arise by isomerization of the alkoxysilanes after reaction, since the ratios of isomers do not change during the course of the reaction, and quite different ratios are obtained for the same alkoxysilane using different amines. The reaction can be envisaged as occuring by way of transition states such as XVIII, XIX (Scheme 2) giving backside attack (and hence inversion stereochemistry, as is frequently observed for the amine-catalyzed alcoholysis [17]), and the Z/E product ratio would be given by k_1/k_2 if K = 1 and the equilibrium is rapidly established. The nature of both alcohol and amine would affect the ratio k_1/k_2, probably mainly through steric factors. Indeed, the bulkier the alcohol used, the greater the preference for E product. which is a reasonable result on steric grounds. Overall rate of product formation should be affected by the basicity of the amine when it is acting as a general base catalyst, but clearly there is no relationship in the present data between Z/E ratio and catalyst basicity. A bias toward Z product is seen

Scheme 2



for both aniline (pKa, $R_3\overset{+}{N}H$ = 4.6) and isopropylamine (pKa, $R_3\overset{+}{N}H$ = 11.5) but not for N-methylaniline (pKa, $R_3\overset{+}{N}H$ = 4.8). It is difficult to see a clear pattern of steric effects for the amines either. Isopropylamine and cyclohexylamine might have been expected to behave similarly from the point of view of steric effects, at least in comparison with a 3° amine like triethylamine. In the methanolysis reaction where appreciable differences in Z/E ratio due to catalyst can be seen, cyclohexylamine is like triethylamine, not like isopropylamine.

Amine playing the role of nucleophilic catalyst can also be envisioned [18] (Scheme 1), and intermediates of the type XIV and XV are presumably present in the process of isomerization of II. However, Scheme 1 offers no obviously better rationale for the effects of amines on Z/E ratios, and it would probably lead to retention stereochemistry, since available information indicates that displacement of leaving groups from axial positions of trigonal bipyramids (XIV → XVI and XV → XVII) occurs with retention [8,19,20]. This stereochemical outcome would apparently be unique to the silacyclopentane system, since

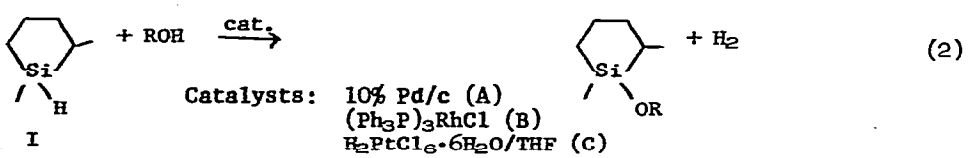
alcoholysis catalyzed by amines normally is stereospecific with inversion [17].

Given the fact that alcoholysis of SiCl is stereoselective, it is not surprising to find that aminolysis is also (Reaction 1, Table 2)

II (1)

Again the apparently thermodynamically more stable E isomer of the silylamine product is formed preferentially, and again we assume that a rapid equilibrium between SiCl isomers (E-II⇌Z-II) and unequal rates of attack on the two is the reason for the stereoselectivity.

Alcoholysis of silicon hydrides catalyzed by transition metals is another method of access to alkoxysilanes. The reactions have been found to be stereospecific by previous workers [21,22], although sometimes weakly so, and in the silacyclopentane system the hydrides (I) can be readily separated into fractions that are predominantly Z or E. Consequently the SiH alcoholysis offered the possibility that alkoxysilanes enriched in either Z or E component could be prepared, a preparative goal which could not be achieved using the stereoselective alcoholysis of SiCl. We have studied the alcoholysis (Reaction 2 and Table 4) of I in the presence of three different catalysts using hydride



I (2)

enriched in either Z or E isomer and using methanol (MeOH), ethanol (EtOH), 2-propanol (iPrOH) and cyclohexanol (cHexOH). Alcoholysis with MeOH or EtOH appears to be a stereoselective reaction favoring E-product to approximately the same extent with both alcohols and all three catalysts. It seems likely that this result is deceiving with respect to the alcoholysis reaction itself, because alcoholysis with iPrOH and cHexOH is clearly stereospecific but followed

by a relatively slow isomerization of the alkoxysilane initially formed. The two columns under IX and XI (Table 4) represent the isomer ratios found at the approximately half-life of the reaction and at a later time when the reaction is essentially complete. The results indicate that the alcoholysis is clearly predominantly, if not completely, stereospecific with inversion with all three catalysts. Previous results of Sommer [21] and Corriu [22] also show a reaction that is not completely stereospecific, presumably indicating that isomerization of alkoxysilane is catalyzed by the transition metals. In the present work it is clear that isomerization of SiH is not occurring during the course of the reaction, as shown by gc analysis of the Z-I/E-I ratio at intermediate times. We presume that the methanolysis and ethanolysis reactions are also stereospecific but that isomerization of methoxy- and ethoxysilane is more rapid than that of the more hindered alkoxysilanes.

The stereochemical result of inversion is the same as that previously observed in acyclic systems for the SiH alcoholysis when the Pd/C or H_2PtCl_6 [21] catalysts are used. Alcoholysis using $(Ph_3P)_3$ RhCl in benzene is reported to proceed with predominant retention [22], however in that work 2-propanol gave racemic product, and methanolysis in MeOH gave inversion. The present result of inversion was not affected by the presence or absence of benzene as solvent. The mechanism suggested [22] for the Rh^I catalyzed alcoholysis involves initial oxidative addition of Si-H to give pentacoordinate Rh^{III}. Next, alcohol can attack, and it is suggested that ROH attacks Si directly without prior coordination to Rh. Perhaps the relatively low stereospecificity of this reaction means that alcohol can either attack directly or after coordination to Rh, with different stereochemical results, and with the favored pathway being a complex function of alcohol structure and concentration as well as silane structure. Interestingly, while in the previous paper in this series [4] we have discussed the possibility that there could be a bias toward retention reactions caused by some angle strain present in the silacyclopentane ring or in the reaction intermediates it forms, the present observation is the first that we know of in Si or P chemistry in which a strained ring species reacts with inversion while acyclic examples proceed with retention. Unfortunately, we were not able to

TABLE 4. PRODUCT RATIOS IN CATALYTIC ALCOHOLYSIS OF 1,2-DIMETHYLSILACYCLOPENTANE (I) BY METHANOL, ETHANOL, 2-PROPANOL AND CYCLOHEXANOL

I		Product Ratio			
		$SiOCH_3$ (VII)[a]	$SiOC_2H_5$ (VIII)[a]	$SiOCH(CH_3)_2$ (IX)[b]	$SiOC_6H_{11}$-cyclo (XI)[b]
Z/E	Catalyst	Z/E	Z/E	Z/E	Z/E
85/15	10% Pd/C	40/60	40/60	80/20 (30/70)	65/35 (35/65)
30/70	10% Pd/C	40/60	40/60	30/70 (30/70)	35/65 (35/65)
85/15	$(Ph_3P)_3RhCl$	40/60	40/60	65/35 (53/47)	55/45 (55/45)
30/70	$(Ph_3P)_3RhCl$	40/60	35/65	30/70 (25/75)	30/70 (30/70)
85/15	$H_2PtCl_6 \cdot 6H_2O$/THF	36/64	33/67	55/45 (30/70)	55/45 (35/65)
30/70	$H_2PtCl_6 \cdot 6H_2O$/THF	37/63	30/70	30/70 (15/85)	35/65 (35/65)

[a] These reactions are rapid, and product ratios remain essentially constant over the course of the reaction.

[b] Ratios not in parenthesis were measured when the reaction was approximately half complete. Ratios in parenthesis were measured after complete reaction.

further explore this phenomenon in the silacyclobutane series, since the ring is opened under the reaction conditions [23].

Regretfully, one of the synthetic goals of the investigation of alcoholyses was not in fact realized. While Z-isomer of the isopropoxy and cyclohexoxysilanes could be shown by NMR to predominate at early stages of the reaction, attempts to isolate mixtures enriched in Z-isomer were not successful due to the relatively rapid isomerization.

A stereoselective reaction of a somewhat different type is afforded by our studies of the lithium aluminum hydride (LAH) reduction of 1-fluoro-1,2-dimethylsilacyclopentane, IV (Reaction 3 and Table 2). The LAH reduction of

(3)

Si-F compounds has been shown to be stereospecific with acyclic derivatives and to proceed with inversion [17a]. Two examples of stereospecific retention are known in cyclic systems, silacyclobutane [7] and a silacyclohexane heavily encumbered with fused aromatic rings [24]. A single example of racemization has been reported [17c], and that is in the system that among those studied is most closely related structurally to the silacyclopentane ring; namely, a silacyclohexene.

The isomers of IV are readily separable by spinning band distillation, and they are much more configurationally stable than the corresponding Si-Cl isomers under a variety of conditions. A number of species do, however, act as isomerizing agents for IV, as observed by NMR. A mixture with an 86/14 Z/E ratio is converted in less than 10 minutes to an approximately 50/50 mixture when added to methanol as solvent present in large excess. Such a racemization [25] or isomerization [26] of Si-F by MeOH has been previously reported and proposed to be occurring by way of extracoordinate Si species. With the mechanistic precedent established for other silicon halides in the presence of other nucleophilic solvents [8,16], and given the results to be presented below, we agree that a mechanism by way of expanded coordination is likely.

Hexamethylphosphorus triamide in CCl_4 also isomerizes IV ($t_{\frac{1}{2}}$ = ca. 2 days), as does tetrabutylammonium fluoride in $CDCl_3$ ($t_{\frac{1}{2}}$ = ca.2 h). Rate data for these systems are only semiquantitative due to the difficulties of integrating poorly separated ^1H NMR peaks for the Si-Me groups of Z- and E-IV. However, the HMPT isomerization proceeds orders of magnitude more slowly for IV than for the corresponding Si-Cl compounds (II).

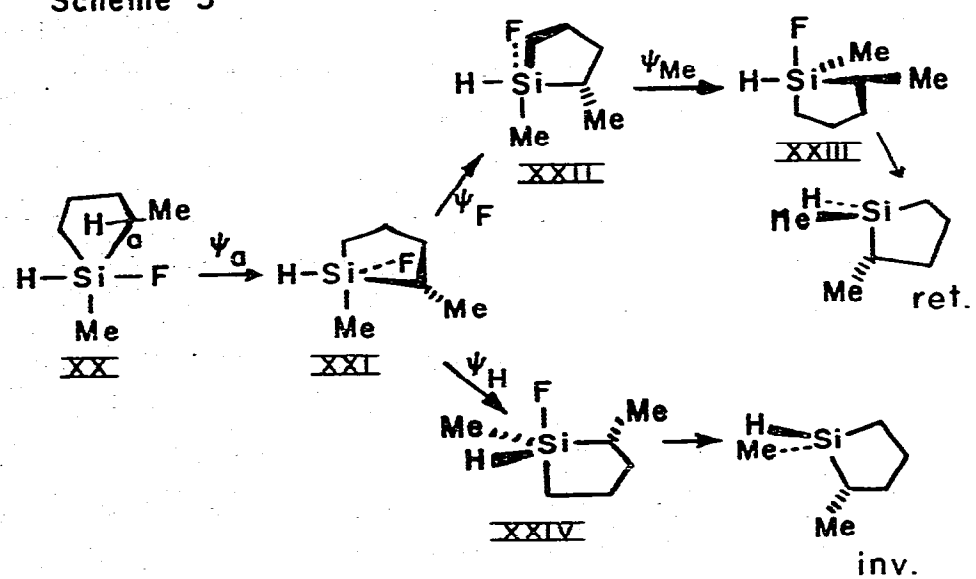
We find that isomerization occurs in the course of LAH reduction of IV. Starting with isomeric mixtures which contain a preponderance of either Z- or E-IV, an approximately 50/50 ratio (Z/E = 47 ± 2/53 ± 2) of silicon hydride (I) isomers is obtained. When the reaction is followed by ^1H NMR, Si-Me peaks characteristic of Z-I and E-I grow in, and they do so as the approximately 50/50 mixture. The ratio of fluoride isomers changes very little as reaction proceeds, indicating that neither aluminum hydride nor aluminum fluoride is isomerizing IV prior to reaction. Silicon hydride is also not being isomerized after it is initially formed. When the reduction reaction is carried to completion and then an extra amount of one of the I isomers is added to the reaction mixture, isomerization of the extra I occurs only slowly. Also in separate experiments, I has been shown to be isomerized only slowly by LAH in ether and not at all by tetrabutylammonium fluoride in $CDCl_3$.

We think it significant that SiF reduction, while normally stereospecific, is reported to proceed with racemization in Corriu's six-membered ring system [17c]. We assume that the mechanisms are related. It is possible to imagine that there are single-step processes occurring which are competing inversions and retentions and that rates fortuitously cancel. In our system the observations made would require the near identity of 4 rate constants. Furthermore, identical rates of inversion and retention would also have to be proposed in the 6-membered ring case. We think this is highly unlikely, particularly in view of the normally high stereospecificity of organosilicon reactions in the absence of some special racemizing process.

The only other reasonable alternative left for the silacyclopentane system, given the lack of isomerization of either starting material or product under the reaction conditions, is irreversible conversion of IV to an intermediate

which can lead to either isomer of I. Since ionization or ring-opening are chemically unreasonable processes under the reaction conditions, we conclude that the intermediate must be one with expanded coordination. We cannot, of course, precisely define the nature of the intermediate, but a 5-coordinate intermediate which undergoes pseudorotations is a reasonable postulate. We believe it is reasonable to propose that pseudorotations will be more readily observable in reactions of silacyclopentanes than in acyclic silanes or silacyclobutanes because axial attack of a nucleophile would lead to an intermediate which would not be especially satisfactory (Scheme 3). That

Scheme 3



intermediate would have either the F or one of the ring bonds axial, and these may well be choices which are not much different in energy. Pseudorotation would presumably be facilitated in order to get away from the initial, unsatisfactory intermeidate (XX) and to get to those with both F and a ring bond axial (XXIII and XXIV), and a single Berry pseudorotation will not suffice to convert XX to either XXIII or XXIV. In contrast to the situation with the silacyclopentane, acyclic systems do not have the strain present in XX which induces pseudorota-

tions, and inversion is observed. In the case of the silacyclobutane, which reacts with retention, the initially formed intermediate is presumably not the analog of XX, but the analog of XXII, which goes to one of the most stable trigonal bipyramids by a single pseudorotation. Hence, the observation of isomerization with IV is the result of the moderate degree of strain in the silacyclopentane ring, and it might be expected that other reactions which involve displacement of relatively poor leaving groups from Si would show a tendency toward isomerization when applied to silacyclopentanes.

CONCLUSIONS

We have developed a number of methods for the preparation of 1,2-dimethylsilacyclopentane derivatives enriched in one of the geometric isomers. In a number of cases, but not those of the alkoxysilanes or silylamines, we can obtain mixtures enriched in either geometric isomer. While stereospecific reactions of the silacyclopentanes show more in common with acyclic silanes in terms of stereochemical outcome, there are notable exceptions. $Rhodium^{I}$-catalyzed alcoholysis of SiH occurs with inversion, while the reaction goes with retention in acyclic silanes. Most notable with the silacyclopentanes is a heightened tendency to give stereoselective reactions or isomerizations. We have shown that this can occur as a result of a) rapid isomerization of starting material, b) rapid isomerization of product, or c) rapid isomerization of an extracoordinate intermediate. Due to the complexity introduced by these multiple possibilities it is not possible at this time to make generalizations about the circumstances under which isomerization can be expected to compete with a stereospecific transformation. We suggest that a balance of factors, principally caused by a moderate amount of ring strain, makes the silacyclopentane system a particularly favorable one in which to look for stereochemical evidence of reactions occurring via extracoordinate intermediates.

Acknowledgement. We wish to thank the National Science Foundation and the Centre National de la Recherche Scientifique for financial assistance.

EXPERIMENTAL

General. General experimental procedures, including analysis by NMR and GLPC, were the same as those reported in the preceding communication [4]. Product ratio were measured by NMR or GLPC, as indicated in the individual experimental sections In many, but not all, cases duplicate runs were made and product ratios were reproducible to ± 2%. Compounds refered to in both papers have been given the sam number.

General Method of Amine-Catalyzed Alcoholysis of Si-Cl (II). The chlorosilane (II, Z/E = 50/50) was dissolved in anhydrous pentane and placed in a round bottom flask equipped with a condenser and an addition funnel. A quantity of alcohol and amine in slight excess in comparison to II was added as a solution in pentane. The solution was then brought to reflux and progress of the reaction was followed by GLPC analysis. The reaction required reflux of from several minutes (MeOH, EtOH) to several hours (iPrOH, cHexOH) to several days (tBuOH). The precipitate of amine hydrochloride was filtered off, washed with pentane and the solution concentrated. All the alkoxysilacyclopentanes obtained (VII to XI) were purified by distillation.

The experiments noted in Table 3 were carried out in the same manner starting with quantities of II of the order of 200 mg, and products were simply analyzed by GLPC on a 20' x 1/4" column of 20% SE 30 on Chromosorb W.

1-Methoxy-1,2-dimethylsilacyclopentane (VII). Reactants: 13.56 g (0.091 mole) of II, 3.21 g (0.100 mole) of methanol and 12.95 g (0.100 mole) of quinoline. Weight of VII obtained: 10.5 g (80%), bp 105-110° (60 mm). Anal. Calcd. for $C_7H_{16}OSi$: C, 58.2; H, 11.1. Found: C, 58.4; H, 11.0%. ^1H NMR (CCl_4, 60 MHz) δ 0.15 and 0.11 (s, relative intensities 35/65, Si-CH_3), 3.43 and 3.36 (s, rel. int. 35/65, OCH_3). ^1H nmr ($CDCl_3$, 90 MHz): δ 0.22 and 0.19 (s, rel. int. 35/65) 3.85 and 3.80 (s, rel. int. 35/65). ^{13}C nmr ($CDCl_3$): δ-3.2 (SiCH_3, Z-VII), -5.3 (SiCH_3, E-VII). Ratio of GLPC retention times at 90°: t_Z/t_E = 0.934.

1-Ethoxy-1,2-dimethylsilacyclopentane (VIII). Reactants: 12.5 g (0.084 mole) of II, 4.25 g (0.092 mole) of ethanol and 11.93 g (0.092 mole) of quinoline.

Weight of VIII obtained: 10.9 g (82%), bp 80-85° (20 mm). Anal. Calcd. for $C_8H_{18}OSi$: C, 60.7; H, 11.4. Found: C, 60.8; H, 11.2%. ^1H nmr (CCl_4, 60 MHz): δ 0.14 and 0.11 (s, rel. int. 30/70, $SiCH_3$), 3.71 and 3.66 (q, J = 7 Hz, rel. int. 30/70, OCH_2). ^1H nmr ($CDCl_3$, 90 MHz): δ 0.19 and 0.17 (s, rel. int. 30/70), 3.59 and 3.55 (q, J = 7 Hz, rel. int. 30/70). Ratio of GLPC retention times at 120°: $t_Z/t_E = 0.932$.

1-Isopropoxy-1,2-dimethylsilacyclopentane (IX). Reactants: 9.70 g (0.065 mole) of II, 4.68 g (0.077 mole) of 2-propanol and 10.06 g (0.077 mole) of quinoline. Weight of IX obtained: 8.7 g (78%), bp 90-95° (15 mm). Anal. Calcd. for $C_9H_{20}OSi$: C, 62.7; H, 11.7. Found: C, 62.4; H, 11.5%. ^1H nmr (CCl_4, 60 MHz): δ 0.15 and 0.11 (s, rel. int. 10/90, $SiCH_3$), ^1H nmr ($CDCl_3$, 90 MHz): δ 0.19 and 0.16 (s, rel. int. 10/90), 4.06 and 4.03 (sept., J = 6 Hz, rel. int. 10/90, OCH), 1.15 (d, $(CH_3)_2C$). Ratio of GLPC retention times, programmed at 2°/min from 100° to 140°: $t_Z/t_E = 0.946$.

1-t-Butoxy-1,2-dimethylsilacyclopentane (X). Reactants: 6.00 g (0.0403 mole) of II, 3.29 g (0.0443 mole) of t-butanol and 5.72 g (0.0443 mole) of quinoline. Weight of X obtained after 3 weeks: 4.9 g (65%), bp 95-100° (15 mm). Anal. Calcd. for $C_{10}H_{22}OSi$: C, 64.4; H, 11.9. Found: C, 64.1; H, 11.8%. ^1H nmr (CCl_4, 60 MHz): δ 0.15 and 0.11 (s, rel. int. 3/97, $SiCH_3$), 1.21 (s, $(CH_3)_3C$). GLPC at 150°: only the peak of isomer E was identified.

1-Cyclohexoxy-1,2-dimethysilacyclopentane (XI). Reactants: 5.00 g (0.0336 mole) of II, 3.70 g (0.0369 mole) of cyclohexanol and 4.77 g (0.0369 mole) of quinoline. Weight of XI obtained: 5 g (70%), bp 125-130° (12 mm). Anal. Calcd. for $C_{12}H_{24}OSi$: C, 67.8; H, 11.4. Found: C, 67.5; H, 11.2%. ^1H nmr (CCl_4, 60 MHz): δ 0.14 and 0.11 (s, rel. int. 7/93, $SiCH_3$); 3.6 (m, OCH). Ratio of GLPC retention times at 170°: $t_Z/t_E = 0.968$.

General Method of Stereoselective Aminolysis of SiCl (II). The chlorosilane (II, Z/E = 50/50) dissolved in pentane was introduced into a flask equipped with an addition funnel and condenser (water-cooled for diethylamine, methanol at -40° for dimethylamine). The solution was stirred mechanically at room temperature. The amine dissolved in pentane was added slowly from a funnel

having a cooling coil. The solution was maintained at reflux, then filtered and distilled.

1-Dimethylamino-1,2-dimethylsilacyclopentane (XII). Reactants: 6.0 g (0.040 mole) of II and 4.5 g (0.1 mole) of dimethylamine. Weight of XII obtained: 4.5 g (70%), bp 91-95° (12 mm). Anal. Calcd. for $C_8H_{19}NSi$: C, 61.0; H, 12.1; N, 8.9. Found: C, 60.9; H, 12.1; N, 9.0%. ^1H nmr (CCl_4, 60 MHz): δ 0.11 and 0.05 (s, rel. int. 35/65, $SiCH_3$).

1-Diethylamino-1,2-dimethylsilacyclopentane (XIII). Reactants: 6.0 g (0.040 mole) of II and 7.3 g (0.1 mole) of diethylamine. Weight of XIII obtained: 5.5 g (75%), bp 113-118° (15 mm). Anal. Calcd. for $C_{10}H_{23}NSi$: C, 64.7; H, 12.5; N, 7.5. Found: C, 64.6; H, 12.6; N, 7.4%. ^1H nmr (CCl_4, 60 MHz): δ 0.10 and 0.05 (s, rel. int. 30/70, $SiCH_3$).

General Procedure for Metal-catalyzed Alcoholysis of 1,2-Dimethylsilacyclopentane (I). The reactions in Table 4 were carried out without solvent by slow addition of alcohol to I in the presence of the catalyst: 10% Pd/C (Fluka Puriss.); tris(triphenylphosphine)rhodium (I) chloride (Merck Schuchardt for synthesis); chloroplatinic acid (Fluka), 0.01 M $H_2PtCl_6 \cdot 6H_2O$ in THF. A micro-scale apparatus consisting of a 5 cm^3 round bottom flask with a condenser topped with a calcium chloride tube and two side arms sealed with rubber septa was purged with argon. I (200 mg, 1.75 mmol) and the catalyst (0.01 to 0.02 mmol) were introduced, and thereafter alcohol (1.75 mmol) was added progressively with a a syringe. The solution was agitated by hand. The evolution of hydrogen took place without the necessity for heating. The analysis of products formed was carried out by GLPC during and at the end of the reaction, as described for the amine-catalyzed alcoholysis.

In the case of alcoholysis in the presence of $(Ph_3P)_3RhCl$, the reactions were also carried out in anhydrous benzene using the conditions described by Corriu and Moreau [22]. The results were comparable to those obtained in the absence of solvent.

Preparation and Attempted Isomerization of 1-Fluoro-1,2-dimethylsilacyclopentane (IV). A mixture of 40.23 g (0.27 mole) of II (Z/E = 55/45) and 27.81 g (0.27

mole) of ZnF_2 was placed in a flask and stirred for 15 min. The reaction mixture was distilled and 8.3 g (0.08 mole) of ZnF_2 was added to the distillate. Redistillation afforded 28 g (79%) of IV (Z/E = 54/46 as determined by nmr), bp 110-111°. Anal. Calcd. for $C_6H_{13}FSi$: C, 54.4; H, 10.0; Si, 21.2. Found: C, 54.4; H, 10.0; Si, 21.4%. MS: 132(51), 104(99), 90(46), 89(100), 63(48), 62(49), 47(48), 32(44), 28(99). The isomers were separated by spinning band distillation. E-IV: ^{1}H nmr (CCl_4): δ 0.21 (d, J = 7.6 Hz, 3H), 0.3-2.02 (m, 10H), 0.96 (d, J = 1.5 Hz). ^{19}F nmr (CCl_4, rel. to $CFCl_3$): δ -163.01 (m). Z-IV: ^{1}H nmr (CCl_4) δ 0.23 (d, J = 7.6 Hz, 3H), 0.34-2.02 (m, 10H), 1.10 (d, J = 7 Hz). ^{19}F nmr (CCl_4, $CFCl_3$): δ -169.23 (septet).

A mixture of 0.38 g (0.0026 mole) of II (Z/E = 80/20) and 0.154 g (0.001 mole) of ZnF_2 was placed in a vial and heated at 78° for 50 min. An nmr spectrum of the product mixture showed unreacted starting material in a Z/E = 54/46 ratio. Nmr spectra taken during the course of the reaction indicated that IV was formed in a Z/E = 54/46 ratio.

A mixture of 0.115 g (0.0011 mole) of IV (Z/E = 80/20) and 0.18 g (0.0014 mole) of ZnF_2 was placed in a nmr tube, heated at 80° for 3h, then allowed to stand at room temperature overnight. An nmr spectrum showed no isomerization of IV.

Reduction of IV with Lithium Aluminum Hydride (LAH). A mixture of 0.27 g (0.002 mole) of IV (Z/E = 5/95), 0.05 g (8 x 10^{-4} mole) of LAH and 2 ml of anhydrous ether was placed in a vial equipped with a septum. The reaction mixture was analyzed immediately after mixing using GLPC (16' x 1/8" 15% Apiezon L on 60-80 mesh Chromosorb W, 115°). Three peaks were observed with retention times (measured from ether signal) of 2.44 (38.9 %), 2.74 (34.3%) and 3.38 (26.7%) min. GC-MS analysis and a comparison of retention times identified the peaks as IV, E-I and Z-I, respectively. The reaction was carried out three additional times with the results shown in Table 2.

Reduction of IV (Z/E = 5/95) was repeated, but with 0.15 ml of I (Z/E = 20/80) added to the starting materials. Immediate GLPC analysis showed formation of a 33/67 ratio of Z-I/E-I. The silicon hydride showed slow continued isomerization, with isomerization being complete after one day. The mixture

was then decanted and nitrogen was bubbled through the liquid to remove most of the ether. The residue was dissolved in CCl_4 and analyzed by NMR. Unreacted starting material had not undergone isomerization.

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