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STEREOCHEMISTRY OF REACTIONS IN THE 1,2-DIMETHYLISILACYCLOPENTANE RING SYSTEM

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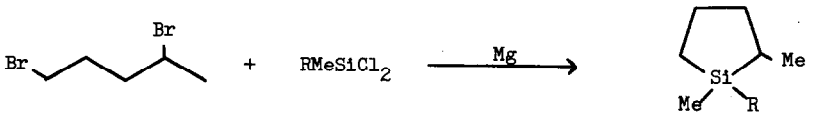
The role of strain in determining the stereochemistry and mechanism of reactions occurring at silicon atoms has been the subject of several recent communications. Stereospecific reactions which occur at Si in the silacyclobutane[1,2] and silaacenaphthene[3] ring systems take place with predominant retention of configuration even when the reactions are ones which show inversion stereochemistry in acyclic and silacyclohexane ring systems. In connection with these studies we thought that significant new information would be available through an investigation of the silacyclopentane ring system. The silacyclopentane ring system itself is presumably not significantly strained; certainly in comparison to the silacyclobutane and silaacenaphthene rings, it is not. Nevertheless, if nucleophilic attack at silicon involves an intermediate (or transition state) which is trigonal bipyramidal, placement of the two ring bonds in equatorial positions in order to have the entering and leaving groups axial for a direct displacement with inversion might be expected to involve substantial strain. Indeed, one of the early "rules" postulated[4] to account for organophosphorus stereochemistry was that five-membered rings (as well as four-membered ones) could be expected to span an axial and an equatorial position in a trigonal bipyramid. Retention is thus the normal stereochemistry for displacement and reduction reactions in four-and five-membered phosphorus rings.[5] Nevertheless, there is a known example involving nucleophilic displacement on a phospholanium ion in which inversion is observed[6] and in which there is presumably an intermediate with the ring bonds both equatorial. We now wish to report that inversion stereochemistry appears to be a normal course for nucleophilic displacement in five-membered silicon rings, in contrast to the results for four-membered rings.

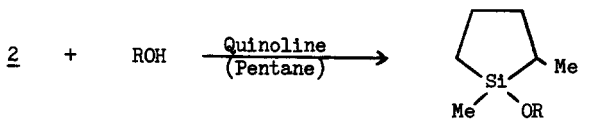
A variety of 2-methylsilacyclopentane derivatives are available through ring closure using 1,4-dibromopentane, a dihalosilane and magnesium in ether.[7] Comparable yields are obtained by mixing all reactants in a single pot or by initial formation of the diGrignard reagent from the dibromide. The mixture of geometric isomers obtained in all of these ring closure reactions



1, R = H
2, R = Cl

has been near to 50/50. The silicon hydride isomers, Z-1 and E-1, can be separated by careful spinning band distillation into fractions of greater than 98% isomeric purity.

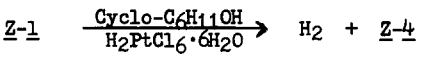
The alcoholysis of 1-chloro-1,2-dimethylsilacyclopentane, 2 (Z/E: 50/50), like the same reaction with the corresponding silacyclobutane,[1] is stereoselective and leads to alkoxy derivatives much enriched in E isomer when the alcohol used is sufficiently hindered.



3, R = CH_3 (Z/E = 30/70)
4, R = cyclo-C_6H_{11} (Z/E = 7/93)
5, R = t-C_4H_9 (Z/E = 3/97)

Proton chemical shifts in 1-5 allow unambiguous structural assignments to be made in a manner analogous to that used previously for the silacyclobutane isomers.[1,2] Methyl groups cis to one another are mutally shielding, while a methyl cis to the SiH proton shields that proton (Table 1).

As with the previously reported silacyclobutanes,[1,2] one can consider two ways of preparing derivatives with stereochemical selectivity. One can carry out a number of stereospecific substitutions at Si, using the hydride isomers, Z-1 and E-1, or using the alkoxides, 3,4 or 5, enriched in E isomer. Alternatively, the Z isomers of the alkoxides are available from the hydride, Z-1, through a catalytic dehydrocondensation:



The stereochemistry of this reaction is inversion, as in the aliphatic series.[8] We have verified the stereospecificity by showing that E-1 produces E-4.[9]

Chlorination of either geometric isomer of 1 produces a pure geometric isomer of 2 in a stereospecific reaction. This reaction has been carried out to obtain significant amounts of

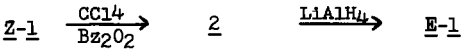


Table 1

NMR Chemical Shifts

Compound	C_2-CH_3	Si-CH_3	Si-H
Z-1 (a)	1.04	0.06	4.01
Z-1 (b)	1.00	0.00	4.15
E-1 (a)	1.07	0.13	3.83
E-1 (b)	1.10	0.06	4.00
Z-2 (a)	1.10	0.49	
E-2 (a)	1.06	0.40	
Z-3 (c)	1.10	0.15	
E-3 (c)	1.05	0.11	
Z-4 (c)		0.14	
E-4 (c)		0.11	
Z-5 (c)		0.15	
E-5 (c)		0.11	

Proton shifts were measured [a] in CCl_4 with benzene (δ 7.24) as internal standard and are reported in ppm downfield from TMS, [b] in C_6H_6 with TMS as internal standard, [c] in CCl_4 with TMS as internal standard.

the pure isomers of 2, which can then be converted back to 1 with lithium aluminum hydride in ether. The sequence of two reactions results in production of Z-1 from E-1 and vice-versa. For reasons stated in detail in our previous communication[2] concerning the same reaction in the silacyclobutane series, we believe the free radical chlorination must be a retention reaction, and thus the hydride reduction is an inversion. This conclusion is also in agreement with the tentative structural assignments one could make on the basis of the small chemical shift differences for the Si-CH_3 and C_2-CH_3 protons in the Z and E isomers of the chloride, 2.

Inversion stereochemistry is normal for the LAH reduction of silyl chlorides in systems other than ring-strained ones or bycyclic ones with bridgehead silicon. The reaction has normally been considered to be a direct displacement of the S_N2-Si type,[10] although recent evidence in the related displacement of chloride by Grignard reagents has been interpreted in terms of slow formation of a pentacoordinate intermediate.[11] Whichever mechanism is operating in the present case, it is reasonable to propose that two silacyclopentane ring bonds are spanning equatorial positions in the intermediate or transition state. If formation of a pentacoordinate intermediate with one ring bond axial were to occur and be followed by pseudorotations, then retention or complete isomerization would be more logical stereochemical outcomes. We are further investigating the influence of entering and leaving groups on the stereochemical pathway in the silacyclopentane system.

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

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