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Preliminary communication

LITHIUM ALUMINUM HYDRIDE REDUCTION OF 1,2-DIMETHYL-1-FLUOROSILACYCLOPENTANE; THE ROLE OF EXTRA-COORDINATE INTERMEDIATES

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Summary

Isomerization occurs in the course of $LiAlH_4$ reduction of the geometric isomers of 1,2-dimethyl-1-fluorosilacyclobutane (I). Neither I nor the hydride product are isomerized under the reaction conditions. The results indicate irreversible formation of an extracoordinate intermediate.

The existence of stable species with 5- and 6-coordinate silicon atoms has for a long time suggested the possibility of the intervention of extra-coordinate intermediates in dynamic processes taking place at silicon in triorganosilanes. Although proposals of such intermediates are frequently made, convincing evidence of their presence has been very sparse. One convincing case is the racemization* or isomerization [2] of silyl halides by polar aprotic solvents, which has been thoroughly investigated. It is possible that reported alcohol-induced racemization [3] and isomerization [4] of silyl fluorides are also such processes. With respect to chemical reactions there is little clear information. There is still debate about the intervention of intermediates in base-catalyzed SiH hydrolysis [5], a system presumably favorable to intermediate formation. Corriu and coworkers have argued vigorously in favor of intermediates in the important reactions of halosilanes with Grignard and organolithium reagents [6]. We now report good evidence for the presence of an extracoordinate intermediate in the lithium aluminum hydride reduction of a fluorosilane.

1,2-Dimethyl-1-fluorosilacyclopentane (I) may be prepared from the previously reported [7] chloro derivative (II) by a ZnF_2 exchange reaction. The reaction, carried out without solvent, affords a constant ratio (Z/E = 54/46) of the geometric isomers of I regardless of the isomer ratio in the

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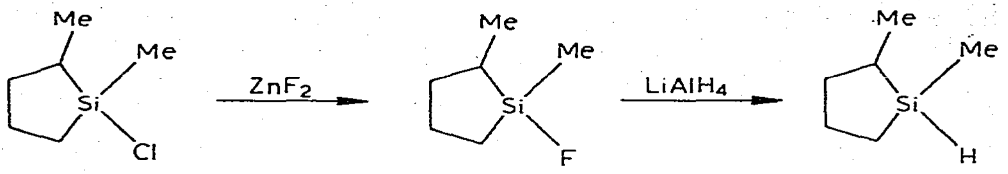
*For a review, including some otherwise unpublished work, see ref. 1.



(II) (I) (III)

starting II, and when the reaction is followed by ^{1}H NMR, isomerization of II is seen to be occurring faster than formation of fluoride I. Isomer ratios were measured by integration of the Si—Me peaks in the NMR spectra of II (reported in ref. 7) and I (δ 0.23 d ppm, J 7.6 Hz for Z-II and δ 0.21 d ppm, J 7.6 Hz for E-II when spectra were measured at 100 MHz in CCl_4 with C_6H_6 as internal reference). Assignment of configuration for the isomers of I was made on the basis of the chemical shifts of Si—Me, C_2—Me (δ 1.105 d ppm, J 7 Hz for Z-II and δ 0.96 d ppm, J 1.5 Hz for E-II, measured as above) and Si—F (δ 169.23m ppm, for Z-II and δ 163.01m ppm, for E-II, measured in CCl_4 with $CFCl_3$ as internal standard) which are sensitive to Me—Me or Me—F steric interactions.

I is readily separable by spinning band distillation into geometric isomers which appear to be indefinitely configurationally stable in the absence of an isomerizing agent. A number of species do, however, act as isomerizing agents, as observed by NMR. A mixture with an 86/14 (Z/E) ratio of I isomers is converted in less than 10 minutes to an approximately 50/50 mixture when added to methanol as solvent present in large excess. Tetrabutylammonium fluoride in $CDCl_3$ isomerizes I slowly ($t_{1/2}$ ca. 2 h), as does hexamethylphosphorus triamide in CCl_4 ($t_{1/2}$ ca. 2 days). At present, rate data for these systems are only semiquantitative due to the difficulties of integrating poorly separated ^{1}H NMR peaks for the Si—Me groups of Z- and E-I.

Most significantly, we find that isomerization occurs in the course of lithium aluminum hydride ($LiAlH_4$) reduction of I. Starting with isomeric mixtures which contain a preponderance of either Z- or E-I, an approximately 50/50 ratio ($Z/E = 47 \pm 2/53 \pm 2$) of silicon hydride (III) isomers is obtained. When the reaction is followed by ^{1}H NMR, Si—Me peaks characteristic of Z-III and E-III 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 I prior to reaction. Silicon hydride (III) 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 III isomers is added to the reaction mixture, isomerization of the extra III occurs only slowly. Also in separate experiments, III has been shown to be isomerized only slowly by $LiAlH_4$ in ether and not at all by tetrabutylammonium fluoride in $CDCl_3$.

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*See ref. 7 for the NMR spectral data for III. There is relatively little overlap of the Si—Me regions of II and III and thus it was convenient to monitor the progress of reaction by NMR. Isomer ratios of the product III were confirmed by GLPC analysis of the product mixture, Z-III and E-III being separable on a 16 ft. by 1/8 in. column of 15% Apiezon L on 60—80 mesh Chromosorb W operating isothermally at 115°C.

We think it significant that SiF reduction, while normally stereospecific*, is reported to proceed with racemization in a six-membered ring system, that system most closely related to the present one structurally [11]. 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 I to an intermediate which can lead to either isomer of III. 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. That 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. Pseudorotations would presumably be facilitated in order to get away from these initial, unsatisfactory intermediates and to get to those with both F and a ring bond axial.

Acknowledgement

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* SiF reduction by $LiAlH_4$ in the silacyclobutane system is a stereospecific retention [8], and retention has also been reported in a silacyclohexane which is heavily encumbered with fused aromatic rings [9]. The reduction in acyclic systems proceeds with inversion [10].