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Rearrangements of α-Halosilanes Induced by Intramolecular Nucleophilic Attack at Silicon

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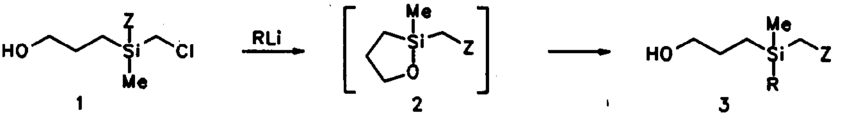
Abstract: Migrations of organic groups from silicon to carbon are facilitated by intramolecular attack by alkoxide at silicon.

In general, nucleophilic displacements at silicon in R_3SiX are considerably more facile than those at carbon in RX. For this reason, we have been interested in the possibility of joining organic fragments by prior attachment to silicon followed by a rearrangement reaction. Wagner-Meerwein-type rearrangements of organosilicon compounds under acidic conditions are well known,[1] and we have found that rearrangements of simple chloromethylsilanes can be carried out under mild conditions using a catalytic amount of $EtAlCl_2$, but that the reaction conditions are incompatible with some substrates.[2]

Rearrangements of α-halosilanes have also been observed under basic (nucleophilic) conditions, usually by using alkoxide or fluoride.[3] In many cases, mixtures of products have been reported, due to competing reaction pathways and instability of the primary products, although choice of solvent and counterion were found to minimize these competing reactions.[3d] We anticipated that rearrangements via *intra*molecular nucleophilic attack (*e.g.*, **1** → **2**) might be faster and cleaner than those involving intermolecular reactions. We report here the use of the γ-oxidopropyl group on silicon as an internal nucleophile to induce rearrangement reactions of organic groups from silicon to an α carbon.

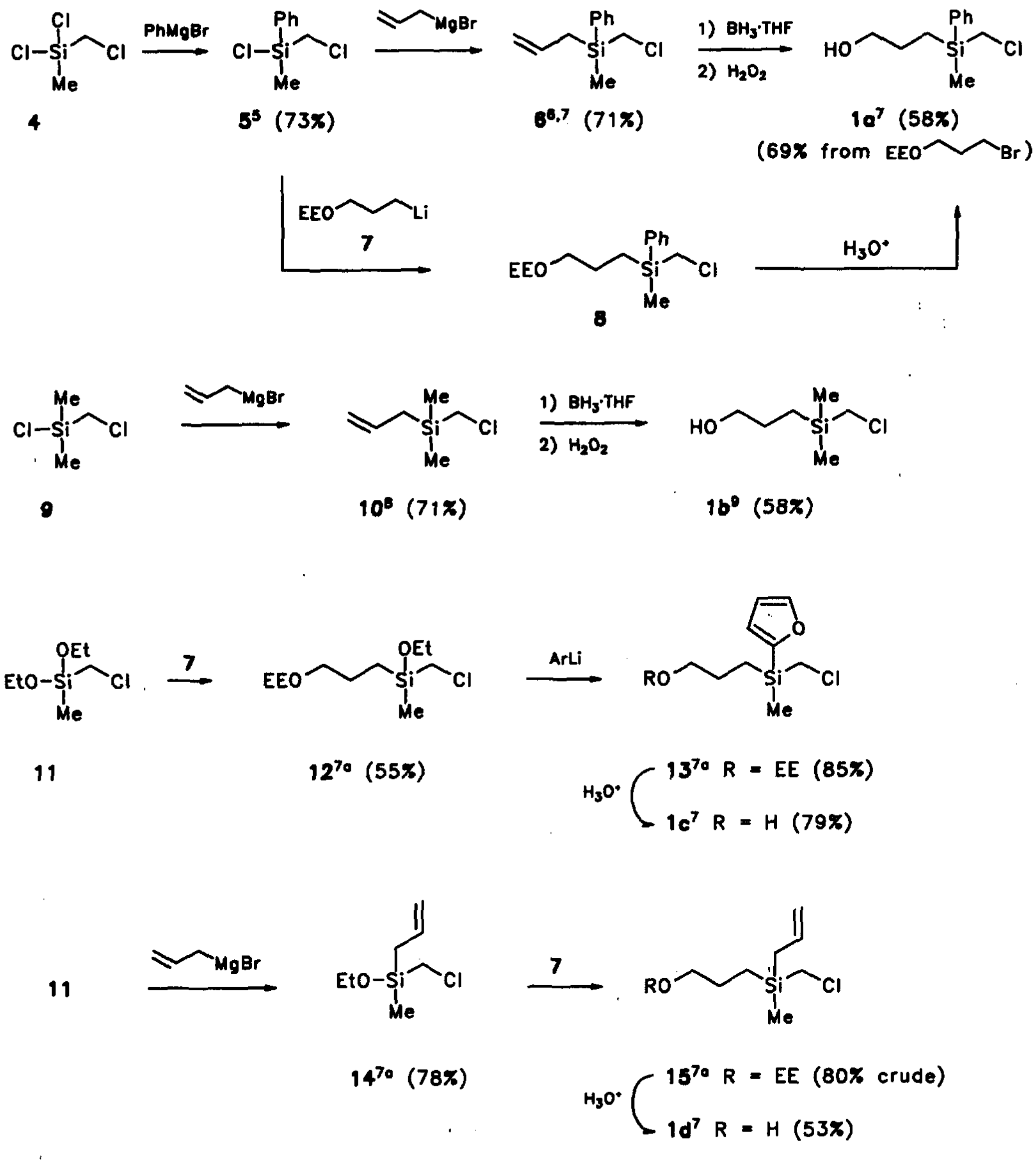


1 2 3

a: Z = Ph; b: Z = Me; c: Z = 2-furyl; d: Z = allyl

As substrates for these rearrangements, γ-hydroxysilanes **1a-d** were prepared from the commercially available chloro- and ethoxysilanes **4**, **9**, and **11**, as shown in Scheme 1. The γ-hydroxypropyl group was introduced by two different methods: by using allylmagnesium bromide followed by hydroboration-oxidation, and by using the ethoxyethyl-protected γ-hydroxypropyllithium reagent (**7**)[10] followed by hydrolysis. The dichlorosilane **4** underwent monoaddition of PhMgBr in good yield, but in other cases (*e.g.*, with 2-lithiofuran) selective monoaddition was not achieved. The diethoxysilane (**11**) gave cleaner products of monoaddition in such cases.[11] It should be noted that in the preparation of substrate **1d**, if the lithium reagent **7** was added to **11** first, the resulting monoethoxysilane was unreactive to allylmagnesium bromide.

Scheme 1[4]



EE = 1-ethoxyethyl

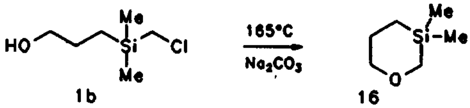
We have studied the reactions of the hydroxypropyl substrates **1a-d** with base. The phenyl substrate **1a** was treated with NaH, KH, Li, and *n*-BuLi in several solvents. In many cases, the starting material was consumed within an hour at room temperature (NaH/THF, NaH/DME, KH/hexane, KH/THF); the less polar systems resulted in slower reactions: *n*-BuLi/ether (5% starting material after 5 h), NaH/ether (complete after 24 h). Most of the reactions appeared clean by GC and GC-MS, but the product, assigned the oxasilacyclopentane structure **2a**[12,13] was not very stable, and additional peaks were observed in the IR (OH) and NMR (CH region) spectra. [Some simple oxasilacyclopentanes have been reported to be unstable, and to undergo reversible dimerization and/or polymerization.[14]] Substrates **1b-d** were also treated with various base-solvent combinations (typically RLi or NaH in ether or THF), similarly resulting in unstable oxasilacyclopentanes (**2b-d**).

When substrate **1a** was treated with 2 equiv of MeLi in ether at room temperature, the ring-opened product **3a** (R = Me)[9b,15] was formed, presumably by trapping of the intermediate oxasilacyclopentane (**2a**) with MeLi. [The structure of the product was proven by comparison with a sample prepared from dimethyldichlorosilane, $PhCH_2MgBr$, and allylmagnesium bromide, followed by hydroboration-oxidation.] Substrates **1b-d** were similarly treated with 2 equiv of RLi at room temperature, giving hydroxypropyl compounds **3b-d**.[16] These compounds were stable with the exception of the 2-furyl compound **3c** (R = Me), which appeared reasonably pure as the crude product, but decomposed upon distillation or chromatography. The results are shown in Table 1.

Table 1

Substrate	Base/solvent	Time	Product	Yield[4]
1a	MeLi/ether	3 h	**3a** (R = Me)[9b,15]	67%
1b	*n*-BuLi/THF	1 h 20 min	**3b** (R = Bu)[7]	84%
1c	MeLi/ether	30 min	**3c** (R = Me)[7a]	88% (crude)
1d	MeLi/THF	10 min	**3d** (R = Me)[7]	66%
1d	*n*-BuLi/THF	30 min	**3d** (R = Bu)[7]	91%

Although we had expected attack at silicon to form a 5-membered ring, we discovered a literature precedent for attack at carbon to form the 6-membered ring: Substrate **1b** has been found to cyclize to the 6-membered heterocycle **16** with slow distillation at atmospheric pressure or by heating with Na_2CO_3.[9] We prepared compound **16** by heating **1b** with Na_2CO_3, and compared it with the product (**2b**) from the reaction of substrate **1b** with 1 equiv of *n*-BuLi/THF (15 min, room temp). None of **2b** was in the product (**16**) from heating **1b** with Na_2CO_3; about 3% of **16** was present in the product (**2b**) from treatment of **1b** with *n*-BuLi/THF at room temperature.



[It should be noted that substrates **1b**, **c**, and **d** have migrating groups which had limitations or were unsuccessful in our rearrangement reactions of simple chloromethylsilanes with $EtAlCl_2$.[2] With methyl as the migrating group (*i.e.*, using Me_3SiCH_2Cl and 0.1 equiv $EtAlCl_2$), no reaction was observed under these conditions or with 1 equiv of $EtAlCl_2$. (Migration of methyl in Me_3SiCH_2Cl has been observed under more vigorous conditions using $AlCl_3$.[1]) With 2-furyl as the migrating group, no reaction was observed using a catalytic amount of $EtAlCl_2$, and decomposition was observed using 1 equiv, possibly due to complexation of the acid at the furyl oxygen; see also ref 3b.) With allyl as the migrating group, a byproduct (about 20% of the product mixture) resulting from cleavage of the allyl group was observed in addition to the expected rearrangement product.[2]]

Migratory aptitudes in rearrangements of halomethylsilanes under basic conditions have been correlated with the ability of the migrating group to stabilize a negative charge.[3c,d,e,g] We were surprised by the facility of methyl migration in substrate **1b**: reaction to form oxasilacyclopentane **2b** was complete at room temperature within 5 min (KH/THF), 15 min (NaH/THF and with *n*-BuLi/THF), and within 2 h (NaH/ether). (With *n*-BuLi in ether, the reaction was slow, with most of the starting material remaining after 3 days.) We believe the idea of using an internal nucleophile to induce rearrangements from silicon to carbon has considerable promise, and we plan to continue to study the scope of this reaction with a view toward using it for forming bonds which may be difficult to form by conventional methods.

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References and Notes

1. Whitmore, F. C.; Sommer, L. H.; Gold, J. *J. Am. Chem. Soc.* **1947**, *69*, 1976-1977. For leading references, see ref 2.
2. Hudrlik, P. F.; Abdallah, Y. M.; Kulkarni, A. K.; Hudrlik, A. M., submitted.
3. For examples and leading references, see: (a) Eaborn, C.; Jeffrey, J. C. *J. Chem. Soc.* **1957**, 137-144. (b) Corey, J. Y.; Corey, E. R.; Chang, V. H. T.; Hauser, M. A.; Lieber, M. A.; Reinsel, T. E.; Riva, M. E. *Organometallics* **1984**, *3*, 1051-1060. (c) Damrauer, R.; Yost, V. E.; Danahey, S. E.; O'Connell, B. K. *Organometallics* **1985**, *4*, 1779-1784. (d) Kreeger, R. L.; Menard, P. R.; Sans, E. A.; Shechter, H. *Tetrahedron Lett.* **1985**, *26*, 1115-1118. (e) Sans, E. A.; Shechter, H. *Tetrahedron Lett.* **1985**, *26*, 1119-1122. (f) Eisch, J. J.; Chiu, C. S. *J. Organomet. Chem.* **1988**, *358*, C1-C5. (g) Aprahamian, S. L.; Shechter, H. *Tetrahedron Lett.* **1990**, *31*, 1089-1092. (h) Matsumoto, K.; Miura, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1991**, *32*, 6383-6386.
4. Yields refer to distilled or chromatographed products unless otherwise indicated.
5. Tamao, T.; Kumada, M. *J. Organomet. Chem.* **1971**, *30*, 349-360.
6. Yoshida, J.; Maekawa, T.; Murata, T.; Matsunaga, S.; Isoe, S. *J. Am. Chem. Soc.* **1990**, *112*, 1962-1970.
7. The (a) IR, NMR, mass spectrum, and (b) exact mass were in agreement with the structure.
8. (a) Connolly, J. W.; Fryer, P. F. *J. Organomet. Chem.* **1971**, *30*, 315-327. (b) Swisher, J. V.; Chen, H.-H. *J. Organomet. Chem.* **1974**, *69*, 93-103.
9. (a) Fessenden, R. J.; Coon, M. D. *J. Org. Chem.* **1964**, *29*, 1607-1610. (b) Dedeyne, R.; Anteunis, M. J. O. *Bull. Soc. Chim. Belg.* **1976**, *85*, 319-331.
10. Eaton, P. E.; Cooper, G. F.; Johnson, R. C.; Mueller, R. H. *J. Org. Chem.* **1972**, *37*, 1947-1950.
11. We have found dialkoxysilanes to be preferable to dichlorosilanes for a number of preparations of tetraorganosilanes. For a different approach, see: Stork, G.; Keitz, P. F. *Tetrahedron Lett.* **1989**, *30*, 6981-6984.
12. Oxasilacyclopentane **2a**: (a) Andrianov, K. A.; Movsumzade, E. M.; Shabanova, D. A.; Shikhiev, I. A. *Dokl. Akad. Nauk SSSR* **1977**, *234*, 1082-1085; *Chem. Abstr.* **1977**, *87*, 102405z. (b) Movsumzade, E. M. *Azerb. Khim. Zh.* **1977**, 65-67; *Chem. Abstr.* **1977**, *87*, 152302j.
13. In some cases, a small amount (>5%) of a second product, assigned as 2-phenyl-2-ethyl-1,2-oxasilacyclopentane (product of methyl migration) was observed in the GC and GC/MS (assigned by the base peak m/z 163 (M^+ - Et) as well as the parent peak m/z 192).
14. Knoth, W. H.; Lindsey, R. V., Jr., *J. Am. Chem. Soc.* **1958**, *80*, 4106-4108. See also Barton, T. J., in "Comprehensive Organometallic Chemistry", Volume 2 (Edited by Wilkinson, G.; Stone, F. G. A.; Abel, E. W.), Pergamon Press, Oxford, 1982, pp 205-303; see p 244.
15. Eaborn, C.; Mahmoud, F. M. S. *J. Organomet. Chem.* **1981**, *209*, 13-16.
16. When substrate **1b** was treated with 2 equiv of MeLi in THF, the expected product **3b** (R = Me) was formed together with $HO-(CH_2)_3-SiMe_3$ in a ratio of 84:16.

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