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Generation of Anionic Intermediates by Intramolecular Nucleophilic Attack at Silicon

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Abstract: *Benzyl and allyl anion equivalents can be generated from benzyl- and allylsilanes by intramolecular alkoxide attack.*

Many useful reactions of organosilicon compounds involve nucleophilic attack at silicon (*e.g.*, generation of reactive anionic intermediates, removal of protecting groups, elimination reactions, *etc.*). Fluoride is often used for these reactions,[1] but it is not always easily obtained and/or kept in anhydrous form, necessary if protiodesilylation is not desired. In addition, any reaction involving *inter*molecular nucleophilic attack on silicon in a complex molecule has the potential problem of control of regioselectivity. We have found that an internal nucleophile on silicon, the γ-oxidopropyl group, is very effective in inducing rearrangements from silicon to carbon.[2] These results suggest that intramolecular nucleophilic attack at silicon might have other applications as well. We report here the use of the γ-oxidopropyl group on silicon for the generation of anionic intermediates.

We expected that a silicon substituted with a γ-oxidopropyl group would be more easily cleaved than a trimethylsilyl group, both from our work on rearrangement reactions,[2] and from the work of Eaborn and Mahmoud, who found that $PhCH_2SiMe_2(CH_2)_3OH$ was cleaved by NaOMe in MeOH at 50°C to form toluene 95-135 times faster than was $PhCH_2SiMe_3$.[3]

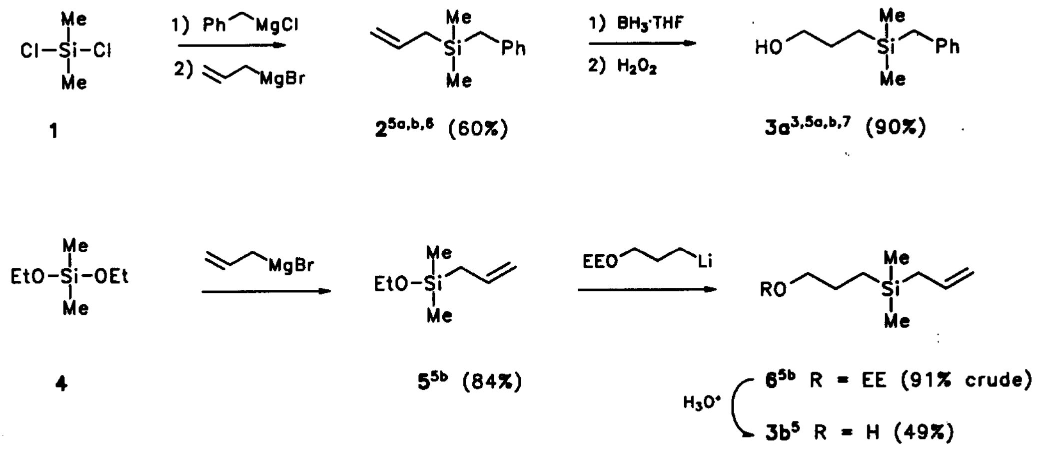
As substrates to test the utility of a γ-oxidopropyl group on silicon for inducing cleavage and the generation of anionic intermediates, γ-hydroxysilanes **3a** and **3b** were prepared, using the commercially available dichloro- and diethoxysilanes **1** and **4** as shown in Scheme 1.

We expected that γ-hydroxysilane **3** when treated with base should initially form the alkoxide **7**, which would be expected to be in equilibrium with the pentacoordinate intermediate **8** and possibly the oxasilacyclopentane **9** and anion Z^-, depending on the system and conditions. In the presence of an electrophilic reagent (E^+), one might observe reaction at oxygen (to form **10**) or at Z to form E-Z (Scheme 2).

We have studied the reactions of γ-hydroxysilane **3a** with several bases and solvents at room temperature. In most cases, **3a** disappeared, with formation of toluene, the product of protiodesilylation: KH/ether (3 min), NaH/THF (30 min), KH/hexane (6 h).[8] With NaH/ether or *n*-BuLi/THF, little or no reaction was observed (4 h and 1 day, respectively).

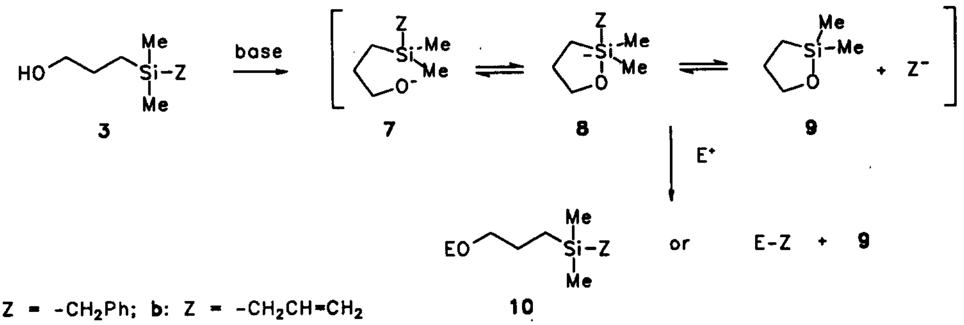
To explore the possibility that substrate **3a** could be used for the generation of a benzyl anion or benzyl anion equivalent, we treated **3a** with NaH/THF in the presence of several electrophiles at room temperature. With the use of benzaldehyde (excess) and of benzophenone, compounds **11**[9,10] and **12**[9], respectively, were observed in the GC and GC/MS together with larger amounts of toluene. In addition, 2,2-dimethyl-1-oxa-2-silacyclopentane (**9**)[11] was observed in the GC/MS. These results demonstrate that

Scheme 1[4]



EE = 1-ethoxyethyl

Scheme 2



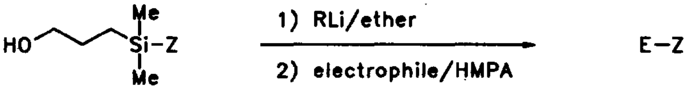
a: Z = $-CH_2Ph$; b: Z = $-CH_2CH=CH_2$

substrate **3a** can function as a benzyl anion equivalent, although trapping with a proton (protiodesilylation) appears to be competitive with trapping with an external electrophile. When **3a** was treated with NaH/THF (5 min) followed by excess MeI, methyl ether **10a** (E = Me) (characterized only by GC/MS[12]) together with comparable amounts of toluene was observed; no ethylbenzene was present.

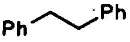
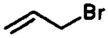
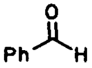
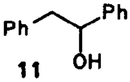
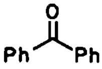
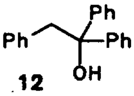
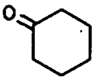
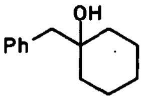
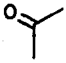
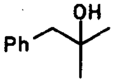
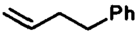
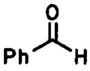
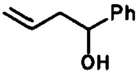
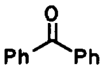
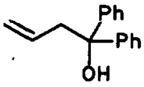
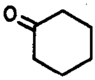
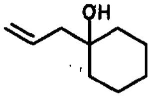
More favorable results for trapping of benzyl with an added electrophile were obtained by treatment of substrate **3a** with MeLi/ether or *n*-BuLi/ether (3-5 min/room temp) (to effect deprotonation) followed by the electrophile in HMPA (10-30 min/room temp). Similarly, substrate **3b** was treated with MeLi/ether followed by several electrophiles in HMPA to give products of trapping of the allyl group. The results are shown in Table 1.

The yields in these reactions have not been optimized. With allyl and benzyl bromides and with nonenolizable carbonyl compounds the reactions worked fairly well; with enolizable carbonyl compounds yields were low. However, the results suggest that a γ-oxidopropyl group on silicon has potential value

Table 1



3a: Z = -CH_2Ph; **3b**: Z = -CH_2-CH=CH_2

Substrate	Electrophile	(equiv)	Product (E-Z)	Yield^{13}
3a		(1.2)		63%
3a		(6.4)		
3a		(1.3)	 **11**	63%
3a		(1.1)	 **12**	63%
3a		(1.1)		14%
3a		(1.4)		21%
3b		(1.0)		59%
3b		(2.9)		
3b		(1.1)		
3b		(1.3)		

for the generation of anionic intermediates, and that a silyl group (such as $\text{-SiMe}_2\text{-(CH}_2)_3\text{-OEE}$) having a protected internal nucleophile could be carried through a synthetic sequence, and then when needed, activated to form a more readily cleaved silyl group ($\text{-SiMe}_2\text{-(CH}_2)_3\text{-O}^-$). We are continuing to study highly reactive silyl groups which can be held in latent form.

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References and Notes

1. Weber, W. P. "Silicon Reagents for Organic Synthesis", Springer-Verlag, New York, NY, 1983; pp 391-404.
2. Hudrlik, P. F.; Abdallah, Y. M.; Hudrlik, A. M. *Tetrahedron Lett.* Preceding communication.
3. Eaborn, C.; Mahmoud, F. M. S. *J. Organomet. Chem.* **1981**, *209*, 13-16.
4. Yields refer to distilled or chromatographed products unless otherwise indicated.
5. The (a) IR, NMR, (b) GC/mass spectrum, and (c) exact mass were in agreement with the structure.
6. (a) Nametkin, N. S.; Vdovin, V. M.; Finkel'shtein, E. Sh.; Oppengeim, V. D.; Chekalina, N. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1966**, 1998-2004; *Chem. Abstr.* **1967**, *66*, 65564u. (b) Jolibois, H.; Doucet, A.; Perrot, R. *Helv. Chim. Acta* **1976**, *59*, 1352-1356.
7. Dedeyne, R.; Anteunis, M. J. O. *Bull. Soc. Chim. Belg.* **1976**, *85*, 319-331.
8. Reactions were run in the presence of a hydrocarbon internal standard; analysis was by GC.
9. Identified by comparison of the GC/MS with that of an authentic sample.
10. Benzyl alcohol was also observed in the GC and GC/MS.
11. Oxasilacyclopentane **9** was identified by comparison of the mass spectrum with literature values: Gu, T.-Y. Y.; Weber, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 1641-1644.
12. Compound **10a** (E = Me): mass spectrum *m/z* (tentative assignment, relative intensity) 222 (M^+, not visible), 207 ($[M - Me]^+$, 0.04), 165 ($PhCH_2(Me)(MeO)Si^+$, 3), 149 ($PhCH_2(Me)_2Si^+$, 2), 131 ($[M - benzyl]^+$, 33), 121 (7), 91 ($C_7H_7^+$, 8), 89 ($Me_2(MeO)Si^+$, 100), 59 (22), 45 (29).
13. All products are known, and spectral values (and in some cases mp) were compared with those of authentic samples. Yields refer to purified products. For runs in which no yield is indicated, the reaction was run in the presence of a hydrocarbon standard, and aliquots were taken. The product was a major component of the GC trace, and was identified by comparison of the GC and GC/MS with that of an authentic sample.

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