Pergamon

Tetrahedron Letters, Vol. 37, No. 37, pp. 6781-6784, 1996

0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)01499-2

Intramolecular Iodosilyletherization of Alkenylsilanols with Bis(2,4,6-trimethylpyridine)iodine(I) Hexafluorophosphate

Koji Takaku, Hiroshi Shinokubo, and Koichiro Oshima*

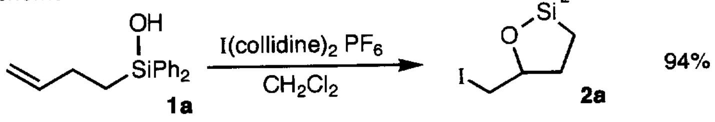
Department of Material Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-01, Japan

Abstract: Whereas iodonium ion-induced intramolecular cyclization of 3-butenyldiphenylsilanol proceeded via *exo* mode cyclization to give 5-iodomethyl-2,2-diphenyl-1-oxa-2-silacyclopentane selectively, iodosilyletherization of 4-methyl-3-pentenyldiphenylsilanol afforded 6,6-dimethyl-5-iodo-2,2-diphenyl-1-oxa-2-silacyclohexane exclusively via *endo* mode cyclization. The oxasilacycloalkanes were converted into the corresponding 1,3-diol and 1,4-diol by oxidative cleavage of the carbon-silicon bond. Copyright © 1996 Elsevier Science Ltd

Various types of organosilicon compounds have been widely used in organic synthesis.[1] Among them, silanols, however, have little synthetic use[2,3] because of their instability[4] and weak nucleophilicity.[5] To our best knowledge, there are few reports on the intermolecular iodosilyletherization[6] and intramolecular iodosilyletherization of alkenes with silanols notwithstanding the numerous examples of intermolecular iodoetherization[7] and intramolecular iodoetherization[8] of alkenes with alcohols. We report herein a simple and effective procedure for preparing 1,3-, 1,4- and 1,5-diols based on intramolecular iodosilyletherization of alkenylsilanols and subsequent oxidative cleavage of the carbon-silicon bond.

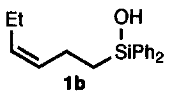
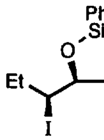
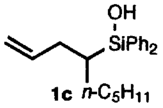
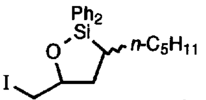
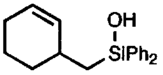
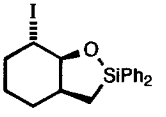
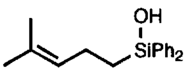
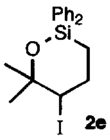
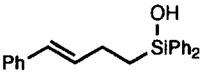
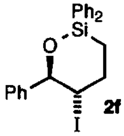
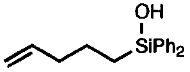
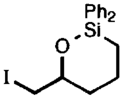
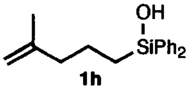
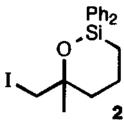
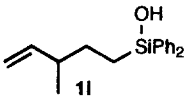
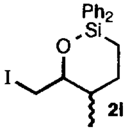
To a solution of 3-butenyl(diphenyl)silanol (**1a**, 0.25 g, 1.0 mmol) in dichloromethane (5 ml) was added bis(2,4,6-trimethylpyridine)iodine(I) hexafluorophosphate [I(collidine)$_2$ PF$_6$][9] (0.67 g, 1.3 mmol) at room temperature under argon atmosphere. After being stirred for 5 h, the mixture was diluted with hexane and the precipitated white solid was filtered through a pad of Celite 545. Concentration of the filtrate in *vacuo* and purification by silica-gel column chromatography gave 5-iodomethyl-1-oxa-2-silacyclopentane **2a** in 94% yield (Scheme 1).

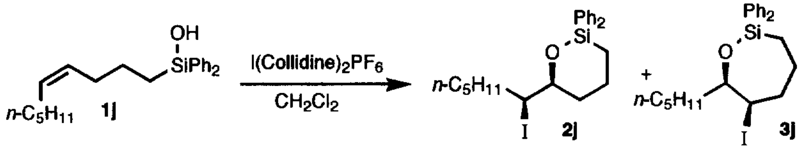
Scheme 1



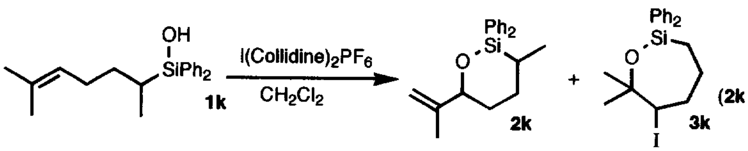
The representative results of intramolecular iodosilyletherization of 3-alkenyl, 4-alkenyl and 5-alkenylsilanols are shown in Table 1. Several comments are worth noting. (1) The reactions of 4-alkenylsilanols proceeded much slower than those of 3-alkenylsilanols. The latter reactions finished within 5 h, but the former did not reach completion after 20 h. (2) Distribution of the products (*endo* cyclization *vs exo* cyclization) heavily depended on the substitution pattern of the olefinic part of alkenylsilanols. In the case of 3- or 4-alkenylsilanols (**1a**, **1c**, **1g**, **1h**, and **1i**) which have terminal alkenes, 5-*exo-trig* mode cyclization[10] or

Table 1. Iodosilyletherization of alkenylsilanols with bis(2,4,6-trimethylpyridine)iodine(I) hexafluorophosphate

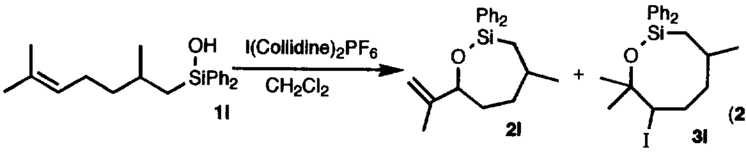
Silanol	Product	Silanol	Product
 **1b**	 **2b** 55%	 **1c**	 **2c** 87%[a]
 **1d**	 **2d** 69%	 **1e**	 **2e** 82%
 **1f**	 **2f** 55%	 **1g**	 **2g** 17%
 **1h**	 **2h** 83%	 **1i**	 **2i** 30%[b]



74%
(**2j** / **3j** = 81/19)



48%
(**2k** / **3k** = 19/81)



35%
(**2l** / **3l** = 22/78)

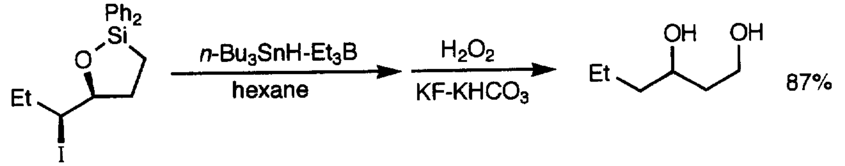
---

[a] isomeric ratio was 72:28. [b] isomeric ratio was 67:33.

6-*exo-trig* mode cyclization proceeded exclusively. (*Z*)-3-Hexenyldiphenylsilanol (**1b**) provided 5-*exo* product as a single regioisomer and (*Z*)-4-decenyldiphenylsilanol (**1j**) gave a mixture of 6-*exo trig* mode cyclization product **2j** and 7-*endo* mode cyclization product **3j** in 74% combined yield (**2j** : **3j** = 81 : 19). In contrast, alkenylsilanols **1e** and **1k** which have two methyl groups on the terminal olefinic carbon preferred *endo* cyclization to *exo* cyclization. For instance, 4-methyl-3-pentenyldiphenylsilanol (**1e**) provided 5-iodo-6,6-dimethyl-2,2-diphenyl-1-oxa-2-silacyclohexane (**2e**)[11] exclusively and 1,5-dimethyl-4-hexenyldiphenylsilanol (**1k**) gave a mixture of *exo* cyclized product **2k**[12] and *endo* cyclized product **3k** in 48% combined yield (**2k** : **3k** = 19 : 81) upon treatment with bis(2,4,6-trimethylpyridine)iodide hexafluorophosphate. *Endo* mode cyclization also proceeded selectively in the reaction of 2,6-dimethyl-5-heptenyldiphenylsilanol (**1l**) to give eight-membered oxasilacyclooctane as the major product (**2l** : **3l** = 22 : 78). Phenyl-substituted alkenylsilanol **1f** provided 6-membered oxasilacyclohexane as a single isomer. 2-Cyclohexenylmethyldiphenylsilanol (**1d**) gave bicyclo[4.3.0] product **2d**. (3) Alkenylsilanols clearly show preference for *endo* mode cyclization over *exo* mode cyclization compared to the iodoetherization of the corresponding alkenols. Whereas intramolecular iodosilyletherization of **1e** provided six-membered ring *endo* product **2e** exclusively, the reaction of 5-methyl-4-hexen-1-ol **4**[13] gave a mixture of oxacyclopentane **5** and oxacyclohexane derivative **6**. Moreover, the reaction of (*Z*)-5-octen-1-ol **7**[13] afforded 2-(1-iodopropyl)-1-oxacyclohexane **8** (*exo* product) exclusively in sharp contrast to the reaction of **1j** giving a mixture of six-membered *exo* and seven-membered *endo* products (**2j** and **3j**) in 81 : 19 ratio. The propensity of alkenylsilanols for *endo* mode cyclization might be attributed to the increased bond lengths of Si-O (1.63 Å) and Si-C (1.89 Å) bonds in silanol compared with those of C-O (1.41 Å) and C-C (1.54 Å) bonds in alcohol. (4) 2-Propenyl(diphenyl)silanol ($CH_2{=}CHCH_2Si(OH)Ph_2$) did not give any cyclization product and allyl iodide was obtained upon treatment with NIS.

The cyclic silyl ethers thus obtained were easily converted into diols by reduction of iodine[14] followed by oxidative cleavage of the Si–C bond[15] as exemplified by the conversion of **2b** into 1,3-diol (Scheme 2).

Scheme 2

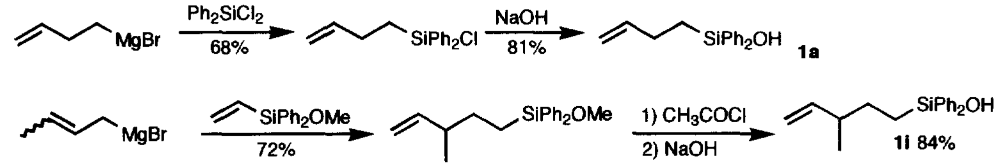


Financial support by Grant-in-Aid for Scientific Research (A) (No, 06403025) and for Encouragement of Young Scientists (No. 08751003) from the Ministry of Education, Science, Sports and Culture, Japan is acknowledged.

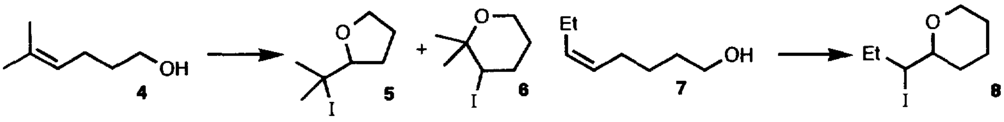
References and Notes

1. Fleming, I. *Organosilicon Chemistry*, in *Comprehensive Organic Chemistry*, Vol. 3, Pergamon Press: Oxford, 1979; Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer- Verlag: New York, 1983; Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: Boston, 1986; Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988.
2. Trost, B. M.; Ito, N.; Greenspan, P. D. *Tetrahedron Lett.* **1993**, *34*, 1421–1424; Soderquist, J. A.; Vaquer, J.; Diaz, M. J.; Rane, A. M.; Bordwell, F. G.; Zhang, S. *Tetrahedron Lett.* **1996**, *37*, 2561–2564.

3. Chan, T. H.; Chen, L. M.; Wang, D.; Li, L. H. *Can. J. Chem.* **1993**, *71*, 60–67; Yamamoto, K.; Kawanami, Y.; Miyazawa, M. *J. Chem. Soc., Chem. Commun.* **1993**, 436–437.
4. Alkenyl(dimethyl)silanols proved to be unstable and were readily converted into water and their disiloxanes in a few minutes. Thus, alkenyl(diphenyl)silanols, which were stable under the reaction conditions, were chosen as substrates. Two general procedures for the preparation of the representative silanols are shown below.



5. Silyl groups reduce the basicity of heteroatoms to which they are directly bonded. Bassindale, A. R.; Taylor, P. G. in *The Chemistry of Organic Silicon Compounds Part 1*, Patai. S.; Rappoport. Z., Eds.; John Wiley & Sons: Chichester, 1989; Chapter 12, pp. 809–838.
6. Treatment of cyclohexene with *N*-iodosuccimide (NIS) and triphenylsilanol in CH_2Cl_2 gave no trace of iodohydrin triphenylsilyl ether. In contrast, the reaction of cyclohexene with NIS and butanol provided 1-butoxy-2-iodo-cyclohexane in 41% yield under the same reaction conditions.
7. Cambie, R. C.; Noall, W. I.; Potter, G. J.; Rutledge, P. S.; Woodgate, P. D. *J. Chem. Soc., Perkin 1*, **1977**, 226–230.
8. Harding, K. E.; Tiner, T. H. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquett, L. A., Eds.; Pergamon Press: New York, 1991; Vol. 4, Chapter 1.9, pp 363–421; Brunel, Y.; Rousseau, G. *Synlett*, **1995**, 323–324; Evans, R. D.; Magee, J. W.; Schauble, J. H. *Synthesis*, **1988**, 862–868.
9. Simonot, B.; Rosseeau, G. *J. Org. Chem.* **1994**, *59*, 5912–5919. In general, bis(2,4,6-trimethylpyridine)iodine(I) hexafluorophosphate gave better yields of oxasilacycloalkane than NIS. For instance, treatment of **1h** with bis(2,4,6-trimethylpyridine)iodine(I) hexafluorophosphate or NIS gave **2h** in 83% or 32% yield, respectively.
10. Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734–738.
11. *5-Iodo-6,6-dimethyl-2,2-diphenyl-1-oxa-2-silacyclohexane* (**2e**): IR (neat) 3064, 3044, 2976, 2928, 1590, 1428, 1383, 1200, 1184, 1145, 997, 902, 786, 739 cm^{-1}; ^1H NMR ($CDCl_3$) 1.29 (ddd, J = 6.2, 7.9, 15.0 Hz, 1H), 1.42–1.52 (m, 1H), 1.47 (s, 3H), 1.49 (s, 3H), 2.44–2.64 (m, 2H), 4.47 (dd, J = 3.3, 8.1 Hz, 1H), 7.34–7.45 (m, 6H), 7.57–7.60 (m, 2H), 7.64–7.67 (m, 2H); ^{13}C NMR (C_6D_6) 10.9, 30.0, 30.9, 31.6, 45.8, 76.5, 128.11, 128.12, 130.1, 130.2, 134.5, 134.9, 136.6, 137.2.
12. Elimination of HI took place under the reaction conditions and isopropenyl-substituted products **2k** and **2l** were obtained instead of 1-iodo-1-methylethyl-substituted products.
13. The reaction of 5-methyl-4-hexen-1-ol **4** with NIS gave a mixture of oxacyclopentane **5** and oxacyclohexane derivative **6** (**5**:**6** = 13:87) in 99% combined yield. Intramolecular iodoetherization of (*Z*)-5-octen-1-ol **7** afforded 2-(1-iodopropyl)-1-oxacyclohexane **8** in 89% yield exclusively.



14. Miura, K.; Ichinose, Y.; Nozaki, K.; Fugami, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.*, **1989**, *62*, 143–147.
15. Tamao, K.; Kakui, T.; Akita, M.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. *Tetrahedron* **1983**, *39*, 983–990; Tamao, K.; Ishida, N.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 2120–2122; Fleming, I. *Chemtracts. Org. Chem.* **1996**, *9*, 1–64.

(*Received in Japan* 24 *June* 1996; *accepted* 29 *July* 1996)