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Stereoselective Synthesis of 1,3-Diol from β-Hydroxyacylsilane via Rearrangement of Phenyl Group from Silicon to Carbon

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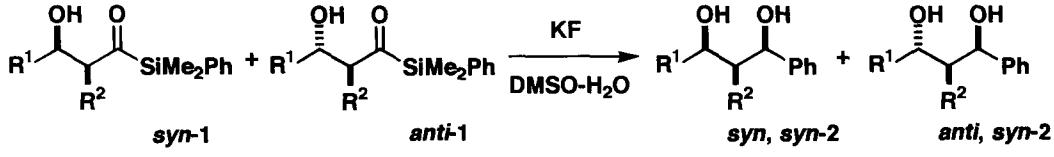
Abstract: Treatment of β-hydroxyacyldimethylphenylsilanes with potassium fluoride in DMSO gave 1,3-diols stereoselectively via migration of phenyl group on silicon.

There are several reports on the migration of one of the alkyl groups from silicon to carbon in a pentacoordinate silicon anionic intermediate which is produced by nucleophilic attack by fluoride ion[1] or alkoxide anion[2] at the silicon atom of acylsilanes. Here we want to report that an addition of fluoride ion to β-hydroxyacyldimethylphenylsilane affords 1,3-diol with high stereoselectivity.

Treatment of β-hydroxyacylsilane **1a** with potassium fluoride in DMSO in the presence of small amount of H_2O[3] for 5 h at room temperature gave 1,3-diol **2a** in 85% yield. Tetrabutylammonium fluoride was equally effective for the rearrangement. Thus, an addition of tetra-butylammonium fluoride to a solution of **1a** in THF at 25 °C gave the same diol **2a** in 77% yield. The representative results with KF are shown in Table 1.

Table 1. Synthesis of 1,3-diol from-β-hydroxyacylsilanes

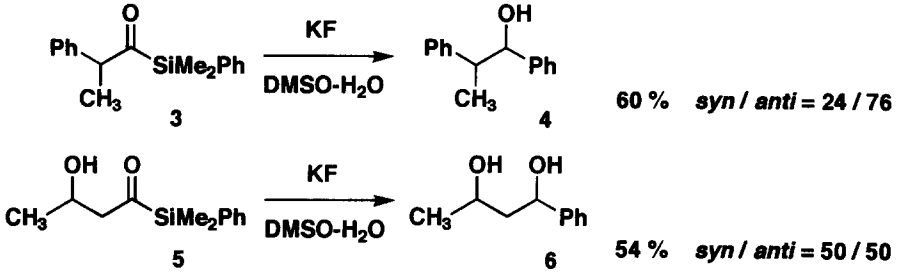


syn-**1** *anti*-**1** *syn, syn*-**2** *anti, syn*-**2**

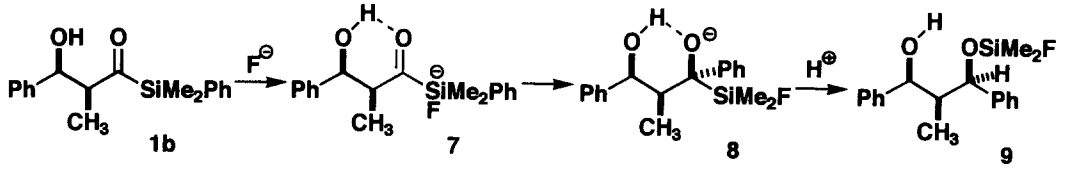
β-Hydroxyacylsilane **1**				Product **2**				
	R^1	R^2	(*syn*/*anti*)		Yield	Isomeric Ratio		
1a	Ph	*n*-C_6H_{13}	85/15	**2a**	85%	85 (*syn,syn*)	14 (*anti,syn*)	<1 (*anti,anti*)
1a	Ph	*n*-C_6H_{13}	22/78	**2a**	81%	22 (*syn,syn*)	66 (*anti,syn*)	12 (*anti,anti*)
1b	Ph	Me	87/13	**2b**	87%	87 (*syn,syn*)	12 (*anti,syn*)	<1 (*anti,anti*)
1c	Me	Me	96/4	**2c**	92%	86 (*syn,syn*)	13 (*syn,anti*)	<1 (*anti,syn*)
1d	*t*-Bu	*n*-C_6H_{13}	100/0	**2d**	81%	>95 (*syn,syn*)	<5 (*syn,anti*)	
1d	*t*-Bu	*n*-C_6H_{13}	0/100	**2d**	33%	100 (*anti,syn*)		

The reaction proceeded stereoselectively in high yields. Whereas *syn*-**1d** gave 1,3-diol (*syn,syn*-**2d**) in good yield with high stereoselectivity, *anti*-**1d** provided the expected 1,3-diol (*anti,syn*-**2d**) in only 33% yield and aldehyde (*t*-BuCH(OH)CH(*n*-C_6H_{13})CHO) was obtained in 25% yield.[4,5]

The presence of both hydroxyl group on β-carbon and alkyl group on α-carbon is essential for the stereoselective formation of 1,3-diol. This was confirmed by the following experiments. Treatment of acylsilane **3** with KF in DMSO provided 1,2-diphenyl-1-propanol **4** in 60% yield as a stereoisomeric mixture of *syn/anti* = 76/24. In addition, stirring a mixture of hydroxy acylsilane **5** and KF in DMSO at room temperature for 6 h gave 1,3-diol **6** in 54% yield as 1:1 diastereomeric mixture.

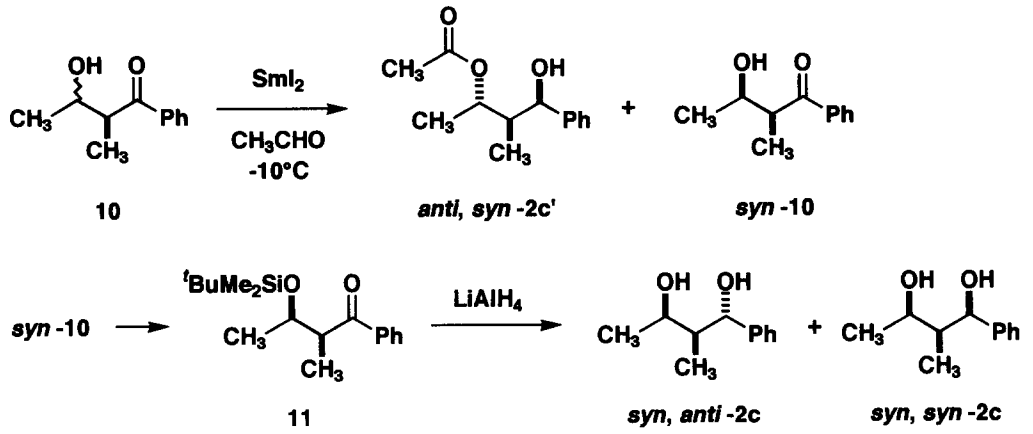


Thus, we are tempted to assume following mechanism for the stereoselective formation of 1,3-diol: (1) β-hydroxyacylsilane might exist predominantly in an intramolecularly hydrogen-bonded form. Fluoride ion attacks silicon atom of acylsilane to provide pentacoordinate silicate **7**, (2) phenyl group migrates from less hindered side of carbonyl group giving **8**, and (3) Brook rearrangement of silyl group from carbon to oxygen under inversion of stereochemistry[6] provides 1,3-diol monosilyl ether **9** which affords **2b** upon workup.



Stereochemical assignment of **2a** and **2b** was performed by comparison with authentic samples prepared according to the reported procedure.[7] Four authentic stereoisomers for **2c** were prepared as follows. Treatment of a diastereomeric mixture **10** (*anti* : *syn* = 1 : 1), derived from acetaldehyde and lithium enolate (PhC(OLi)=$CHCH_3$), with 4 equiv of acetaldehyde and 15 mol% SmI_2[8] in THF at −10 °C resulted in the formation of the *anti*-1,3-diol monoester (*anti,syn*-**2c'**) along with *syn*-β-hydroxy ketone (*syn*-**10**) which was recovered completely unchanged. Hydrolysis of the monoester **2c'** with K_2CO_3 provided *anti,syn*-**2c**. The recovered *syn*-β-hydroxy ketone (*syn*-**10**) was transformed into *tert*-butyldimethylsilyl ether **11** upon treatment with *t*-$BuMe_2SiCl$ and imidazole. 1,2-*Anti* diastereoselective reduction[9] of **11** with lithium aluminum hydride gave a mixture of *syn,anti*-**2c** and *syn,syn* -**2c** (*syn,anti* : *syn,syn* = 9 : 1). Reduction

of **10** with lithium aluminum hydride afforded the fourth diastereomer *anti,anti*-**2c** in addition to three other diastereomers.[10,11,12]



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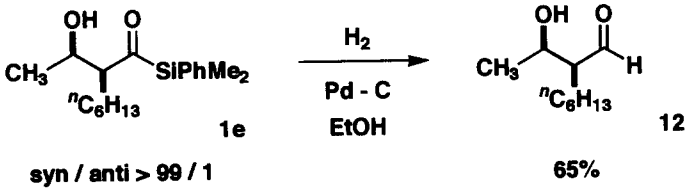
3. The use of D_2O instead of H_2O gave the corresponding 1,3-diol **2a** (PhCH(OH)CH(*n*-C_6H_{13})CD(OH)Ph) bearing deuterium in place of hydrogen (>95% D).
4. Hydrogenation of **1** (H_2, Pd/C) provided aldehyde $R^1CH(OH)CHR^2CHO$ with retention of stereochemistry (Cirillo, P. F.; Panek, J. S. *Tetrahedron Lett.* **1991**, *32*, 457–460; Cirillo, P. F.; Panek, J. S. *J. Org. Chem.* **1994**, *59*, 3055–3063). For instance, hydrogenation of **1e** in the presence of Pd/C catalyst gave *syn,anti*-aldehyde **12** in 65% yield: ^1H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.12–1.48 [m, 11H, including 1.24 (d, *J* = 4.1 Hz, 3H)], 1.57 (m, 1H), 1.73 (m, 1H), 1.95 (bs, 1H), 2.38 (ddt, *J* = 2.2, 9.0, 4.1 Hz, 1H), 4.13 (dq, *J* = 4.1, 6.4 Hz, 1H), 9.77 (d, *J* = 2.2 Hz, 1H).



5. A preparative method of α,β-unsaturated aldehydes via β-alkoxyacylsilanes has been reported. Sato, T.; Arai, M.; Kuwajima, I. *J. Am. Chem. Soc.* **1977**, *99*, 5827–5828.
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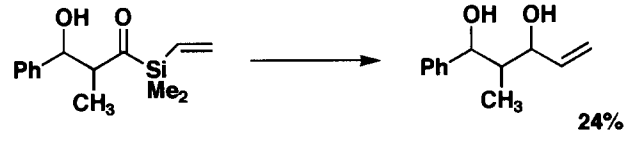
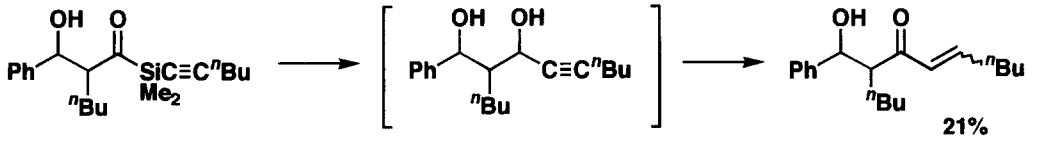
10. ^{1}H NMR ($CDCl_3$) data for **2c** were as follows. *anti,syn*-**2c**: δ 0.82 (d, J = 6.9 Hz, 3H), 1.32 (d, J = 6.6 Hz, 3H), 1.86 (m, 1H), 2.45 (bs, 1H), 3.03 (bs, 1H), 3.84 (m, 1H), 5.11 (d, J = 3.0 Hz, 1H), 7.20–7.40 (m, 5H). *anti,anti*-**2c**: δ 0.56 (d, J = 6.9 Hz, 3H), 1.25 (d, J = 6.3 Hz, 3H), 1.85 (m, 1H), 3.30 (bs, 2H), 3.90 (dq, J = 7.4, 6.0 Hz, 1H), 4.53 (d, J = 9.1 Hz, 1H), 7.20–7.40 (m, 5H). *syn,syn*-**2c**: δ 4.24 (dq, J = 1.8, 6.9 Hz, 1H), 5.05 (d, J = 3.3 Hz, 1H), other signals could not be determined. *syn,anti*-**2c**: δ 0.83 (d, J = 6.9 Hz, 3H), 1.23 (d, J = 6.6 Hz, 3H), 1.40 (bs, 1H), 1.96 (m, 1H), 3.00 (bs, 1H), 4.05 (dq, J = 2.4, 6.3 Hz, 1H), 4.72 (d, J = 7.2 Hz, 1H), 7.20–7.40 (m, 5H).
11. Four diastereomers of **2d** were prepared in similar fashion. ^{1}H NMR ($CDCl_3$) data for C<u>H</u>(OH)Ph are as follows. *syn,syn*-**2d**: δ 4.94 (d, J = 3.2 Hz); *syn,anti*-**2d**: δ 5.01 (d, J = 1.8 Hz); *anti,syn*-**2d**: δ 5.39 (d, J = 1.1 Hz); *anti,anti*-**2d**: δ 4.75 (d, J = 8.9 Hz).
12. Rearrangement of alkenyl group and alkynyl group has been examined. Treatment of acylsilane **13** or **15** with potassium fluoride provided the corresponding migrated products as shown below. However, their migration did not proceed effectively compared to the migration of phenyl group. In the latter case, the corresponding diol could not be detected and the isomerization of propargylic alcohol to enone **16** took place under the reaction conditions.



13 **14**



15 **16**

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