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Priority communication

Migration of aryl groups from silicon to carbon in α,β-epoxysilanes. A new model for hypervalent silicon study

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Abstract

The reaction of (2*R*,3*R*)-3-(triphenylsilyl)glycidol (**1**) with *n*-$Bu_4NF\cdot 3H_2O$ in THF, followed by treatment of the product with *p*-nitrobenzoyl chloride yields (2*S*)-glycidol *p*-nitrobenzoate (**4**) and *trans*-cinnamyl *p*-nitrobenzoate (**6**) in a ratio of 1:1.5. The reaction of (*R*)Si-(2*R*,3*R*)- or (*R*)Si-(2*S*,3*S*)-3-[(methyl)(phenyl)(1-naphthyl)silyl]-glycidols, **7** or **8** respectively, with *n*-$Bu_4NF\cdot 3H_2O$ affords mixtures of the respective glycidol, *trans*-cinnamyl alcohol and 3-(1-naphthyl)allyl alcohol. No significant difference in the product distribution in reaction of these two diasteromers was observed. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: α,β-Epoxysilanes; Aryl group migaration; Hypervalent Si species

1. Introduction

There is continuous interest in hypervalent organosilicon species and the search for models that would make possible a study of stereomutation in various reactions involving transmission between four- and five- (or six-) valent silicon atom [1]. The reaction of (chloromethyl)-silanes with alkoxides or a fluoride anion is known to involve an attack of the nucleophile on the silicon atom, generating a hypervalent intermediate which subsequently disproportionates with an alkyl group migration from silicon to carbon and expulsion of chlorine [2]. Related α,β-epoxysilanes (which embrace a chiral center in the α-position) react with a range of nucleophiles regioselectively via an 'α-opening pathway' [3]. Directing effect of the silyl group, in certain cases overriding considerable steric shielding, has been rationalized by initial coordination of the nucleophile to the silicon atom [4]. However, all attempts including a very recent one [5] failed to provide experimental evidence for the formation of hypervalent silicon intermediates. Now, we report on the first examples [6] of nucleophile-induced aryl groups migration from silicon to the α-carbon atom in α,β-epoxysilanes and on some stereochemical implications of nucleophilic substitution on a chiral silicon atom in α,β-epoxysilanes involving the (methyl)(1-naphthyl)(phenyl)-silyl group.

2. Results and discussion

The reaction of (2*R*,3*R*)-epoxysilane [7] **1** (97:3 enantiomer ratio by HPLC using a chiral column [8]) (Scheme 1) with *n*-$Bu_4NF\cdot 3H_2O$ in THF at room temperature for 6 h followed by in situ derivation of the product with *p*-nitrobenzoyl chloride [9] (to avoid losses of the volatile material) yielded two major products. After flash column chromatography (*S*)-glycidol *p*-nitrobenzoate **4** [10] and *trans*-cinnamyl alcohol *p*-ni-

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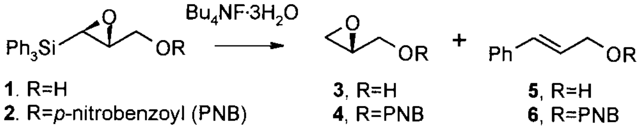
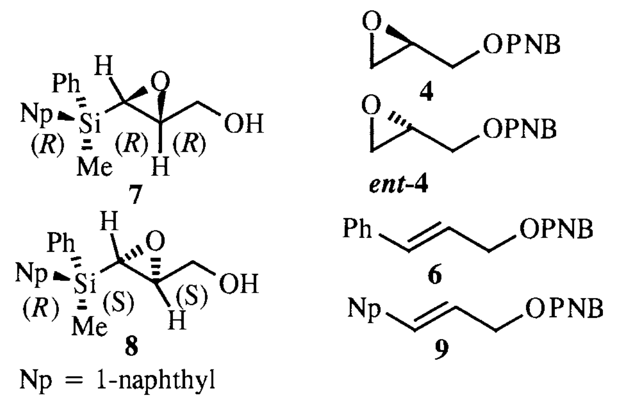


Scheme 1.

trobenzoate **6** were isolated in 53 and 35% yield, respectively. The esters were accompanied by small amounts (2–4%) of the corresponding free alcohols, **3** and **5**, which reflects incompleteness of esterification.

While glycidol **3** was the expected product of the epoxysilane **1** protio-desilylation which is well documented [11], cinnamyl alcohol (**5**) had to result from the phenyl group migration from silicon to carbon. A plausible mechanism for such transformation is depicted in Scheme 2. The addition of fluoride anion to the silicon atom generates the hypervalent silicon derivative (i) which rearranges with the phenyl group migration to the α-carbon atom and simultaneous epoxide ring opening to give β-hydroxysilane (ii). The terminating stage of the rearrangement involves the fluorodiphenylsilanolate elimination. It is noteworthy that protio-desilylation reactions of (triphenylsilyl)oxirane [7](a) and its deuterated analogue [11](a) have been reported to yield oxirane and deuterated oxirane (60% [7](a)), respectively; no other products have been detected.

We examined first the effect of the solvent on the reaction of **1** with a fluoride anion using additionally DMSO, DMF and MeCN, and isolating the products after derivation with p-nitrobenzoyl chloride. In a parallel series of experiments, the PNB derivative **2** was treated with n-Bu$_4$NF under similar conditions. The results are summarized in Table 1.

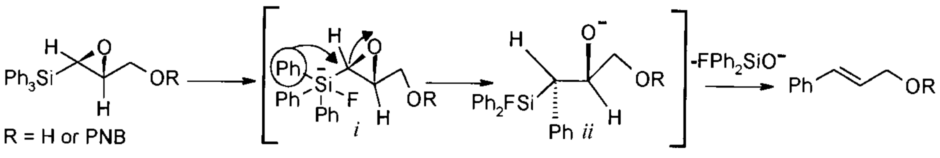


Reaction of epoxysilanes with n-Bu$_4$ NF in THF followed by derivation with PNB chloride

Epoxide	Products	**4**, **6** and **9** ratio	Total yield
7	**4**,**6**,**9**	52.5 : 6.6 : 1	54%
8	*ent*-**4**,**6**,**9**	45 : 6.5: 1	54%

Scheme 3.

As it can be seen from Table 1, in both examined compounds in all solvents examined the product of phenyl group migration was obtained. Free alcohol **1** appeared to be more prone to the rearrangement than its PNB derivative **2**. Taking separately epoxysilanes **1** or **2**, there was virtually no difference between reactions



Scheme 2.

Table 1
Reaction of epoxysilanes with Bu$_4$NF·3H$_2$O in various solvents: yields and products ratio

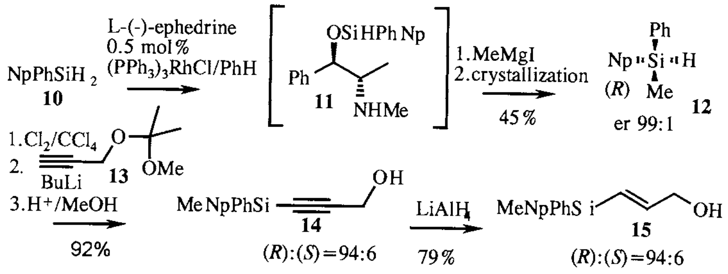
	Epoxysilane	The solvent	Products		Yield (%)a	4:6 ratio[b]
1	1	THF	4	6	88	1:1.5
2		DMSO			81	1:1.8
3		DMF			74	1:0.4
4		MeCN			58[c]	1:1.7
5	2	THF	4	6	76	1:0.25
6		DMSO			60	1:0.25
7		DMF			64	1:0.12
8		MeCN			73[d]	1:0.2

[a] The experiments were performed in the 0.1 mmol scale. Reaction of 1 with fluoride was followed by in situ derivation of the products with p-nitrobenzoyl chloride. Yields refer to isolated product mixtures.

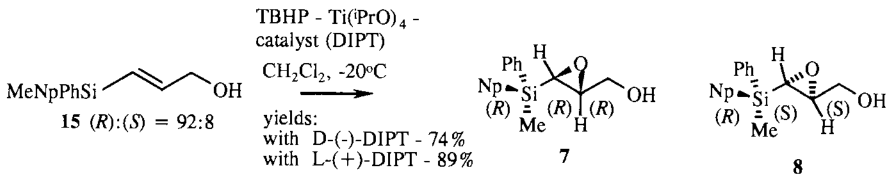
[b] The ratios were determined by HPLC analysis (uv detector 254 nm) of the crude mixtures.

[c] Allyl p-nitrobenzoate was isolated as an additional product (ca. 20% yield)(see the text).

[d] Allyl p-nitrobenzoate was the major product, isolated in ca. 60% yield.



Scheme 4.



Scheme 5.

in THF or DMSO (Table 1, entries 1 and 2, and respectively, 5 and 6). In DMF a markedly smaller amount of the allylic alcohol was generated (entries 3 and 7). When the reaction was carried out in acetonitrile [12] the product consisted of **4** and **6** and the third component which was identified as allyl *p*-nitrobenzoate [13] (ca. 20 and 60% yield from **1** or **2**, respectively). Proportions of **4** and **6** are shown in Table 1 (entries 4 and 8).

It was thought of interest to determine the fate of the aromatic substituents in (methyl)(1-naphthyl)(phenyl)-silylglycidols **7** and **8** (Scheme 3). Two aryl groups with a similar ability to stabilize the negative charge (which is an important factor ([2]b,h) influencing the 'migratory aptitude') but considerably differing in the steric bulk are present in each of these compounds, 1-naphthyl and phenyl. On the other hand, two diastereomers differing in relative configuration around the silicon and the α-carbon atom *lk* (**7**) and *ul* (**8**) atom are accessible for study (vide infra).

Epoxysilanes **7** and **8** (for synthesis of these compounds, [14] vide infra) were treated with n-$Bu_4NF \cdot H_2O$ in THF at room temperature for 16 h and the product was isolated by chromatography and the components ratio was determined by HPLC. The results are presented in Scheme 3. As it can be seen from the scheme, the products of phenyl as well as naphthyl group migration were obtained (**6** and **9**, respectively) in both cases. The product of phenyl group migration clearly dominates. The ratio of phenyl- and naphthyl-derivatives (**6** and **9**) is virtually the same regardless of the epoxide configuration. The apparent lack of memory in the products with respect to the initial relative configuration of epoxysilanes suggests that aryl group migration is not simultaneous with the fluorine anion addition. It is likely that the fate of the initially formed five-coordinated silicon species may be followed by NMR, for which our model is suitable.

The diasteromeric epoxysilanes **7** and **8** were synthesized using optically active allylic alcohol **15** as the common intermediate (Scheme 4). (1-Naphthyl)phenylsilane [15] **10** was treated with (1*R*,2*S*)-(−)-ephedrine in the presence of the Wilkinson catalyst according to Corriu and Moreau [16] to afford the derivative **11** as a mixture of diastereomers. The crude mixture was treated with an excess of methyl magnesium iodide to yield methylnaphthylphenylsilane **12** (90% yield, er (*R*):(*S*) = 79:21 by HPLC). After several crystallizations from pentane virtually optically pure [17] (*R*)-(+)-**12** was obtained ($[\alpha]^{20}_{D} = +34.4$, er 99:1,

Table 2
Assymetric catalytic epoxidation of **15**, (*R*):(*S*) = 92:8 under Sharpless conditions using diisopropyltartrates

Catalyst	Product			
	7 Si (*R*); (1*R*,2*R*)	**8** Si (*R*); (1*S*,2*S*)	Si (*S*); (1*S*,2*S*)	Si (*S*); (1*R*,2*R*)
D-(−)-DIPT	41.81 min	44.85 min	—	49.49 min
	89%	3.5%	—	6.8%
L-(+)-DIPT	41.33 min	44.26 min	35.92 min	—
	2.5%	90.9%	6.5%	—

Diasteromer content and retention times (chiral column with a precolumn [8], hexane-isopropanol (5%), flow 0.5 ml min^{-1}, detection UV at 286 nm).

by HPLC). Pure silane **12** was chlorinated (retention of configuration [15]) and the chloride was reacted with an anion generated from the acetylene derivative **13** to yield, after hydrolysis, **14** with the er of 96:4 (by HPLC). Configuration around the silicon atom in the prevailing enantiomer of **14** has been ascribed as (*R*) since the intermediate silyl chloride is known to react with lithioorganic reagents with inversion of the configuration [18]. Reduction of the triple bond in **14** with lithium aluminum hydride afforded allylic alcohol **15** (79%, er 96:4).

Catalytic asymmetric epoxidation [9] of **15** (Scheme 5) using diisopropyl D-(−)-tartrate (DIPT)(99% ee, Aldrich®) followed by flash chromatography afforded the product in 74% yield, consisting of three components in a ratio shown in Table 2 (determined by HPLC on chiral column [8], the mixture was inseparable by HPLC on a Nucleosil column). Epoxidation of **15** with L-(+)-DIPT (99% ee) as the catalyst yielded a mixture of epoxides in 89% yield (Table 2). Structure assignments were made on the grounds of the rules governing the Katsuki–Sharpless epoxidation [19] and were confirmed by rotation of glycidol *ent*-**4** obtained after protio-desilylation (see above).

3. Conclusion

In conclusion, α,β-epoxysilanes bearing an aromatic group on the silicon atom, on treatment with n-Bu_4NF undergo a rearrangement with the aryl group migration from silicon to carbon. Epoxysilanes with (methyl)(1-naphthyl)(phenyl)silyl group in this reaction afford products of phenyl- and naphthyl-group migration, the former prevailing. No differences could be noted in the reactions course of two diastereomeric epoxysilanes differing in the relative configuration around the silicon and the neighboring carbon atom.

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