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The regiochemistry and stereochemistry of α,β-epoxysilane ring opening with silyl halides or pseudohalides†

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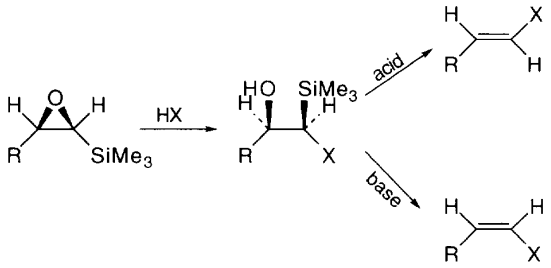
Summary – The reaction of trimethylsilyl halides with α,β-epoxysilanes leads to either a vinyl halide by addition/elimination or a vinyl enol ether by rearrangement; the route depends upon the nature of the groups attached to the epoxide ring. With groups β to the silicon that can stabilise an adjacent positive charge the directive effect of silicon towards substitution at the α position is overcome such that the enol ether is obtained. Trimethylsilyl pseudohalides behave similarly except that the intermediate addition product can be isolated. The stereoselectivity of ring opening is found to vary with the reagent.

epoxide / epoxysilane / ring opening / regiochemistry / halosilane

Introduction

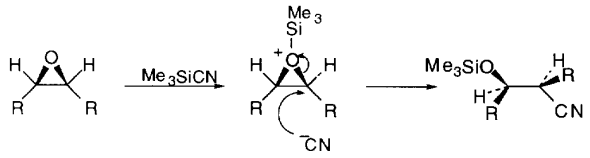
α,β-Epoxysilanes are versatile intermediates for the regio- and stereospecific synthesis of olefins and carbonyl compounds [1]. Hudrlik has shown that α,β-epoxysilanes undergo ring-opening reactions with electrophilic reagents such as Brønsted and Lewis acids *via* complexation at the oxygen followed by nucleophilic attack at the carbon atom α to the silicon, from the opposite side to the oxygen [2].



Scheme 1

It has also been shown that the formation of olefins from the resulting β-hydroxysilanes is highly stereospecific and that a *syn* process takes place under basic conditions and an *anti* process under acidic conditions [3]. Thus, by controlling the reaction conditions, either olefin stereochemistry can be obtained from a single epoxide.

The ring opening of epoxides has also been reported using silyl halides or pseudohalides [4-9]. In this case complexation of the oxygen by the silicon is followed by nucleophilic attack at the less substituted carbon of the epoxide.



Scheme 2

To our knowledge the product distribution and directing effect of the silicon in an α,β-epoxysilane on the ring-opening reaction using silyl halides and pseudohalides has not been investigated. Our work in this area has revealed that both substrate and reagent structure can drastically alter the mechanism leading to a change in both regio- and stereochemistry.

Results and Discussion

Our results are shown in Table I. The reaction of the α,β-epoxysilanes **1** and **2** with trimethylsilyl halides leads to the corresponding vinyl halides, via halide ion attack α to the silicon. However, unlike the reaction using hydrogen halides [1], the transformation was not stereospecific. A 22:78% *Z*/*E* mixture of the 3-phenyl-

† Dedicated to Professor Raymond Calas in recognition of his outstanding contribution in the field of organosilicon chemistry.

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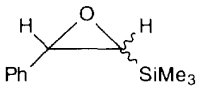
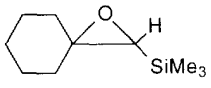
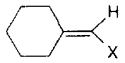
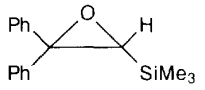
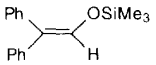
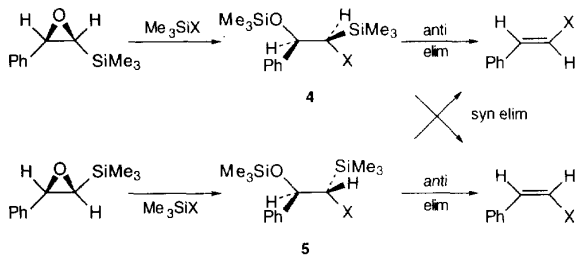
Table I. Products from the addition of trimethylsilylhalides or pseudohalides to α,β-epoxysilanes.

Substrate	Reagent (TMSX)	Product	Yield % (NMR)
	Cl	PhCH=CH-Cl only *E*	99
	Br	PhCH=CH-Br only *E*	98
	I	PhCH=CH-I only *E*	96
1	CN	Ph(Me$_3$SiO)CHCH(SiMe$_3$)CN	41
22:78 *Z*/*E*	N_3	Ph-CH=CH-N_3 25:75 *E*/*Z*	50
	Cl		70
	Br		75
	I		78
	CN		50
2	N_3		46
	Cl		99
	Br		98
	I		98
	CN		97
3	N_3		99

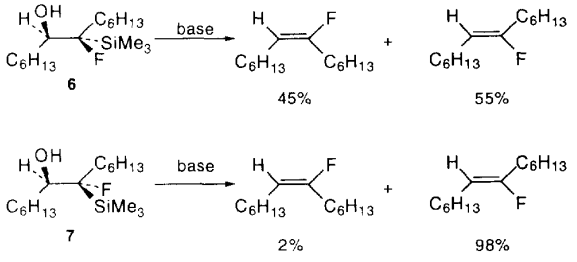
2-trimethylsilyloxirane gave nearly a quantitative yield of *E*-2-halo-1-phenylethene. *Anti* addition of the trimethylsilyl halide followed by *anti* elimination of hexamethyldisiloxane should have given a 22:78% *E*/*Z* mixture of the alkene.



Scheme 3

NMR analysis of the reaction mixture showed the presence of both the intermediates **4** and **5**, indicating that the addition of the silyl halide remained stereoprecise. The presence of only the *E* isomer of the product alkene could arise from subsequent isomerisation of the *Z* alkene under the conditions of the reaction. Alternatively a mixture of *syn* and *anti* elimination could occur, depending upon the intermediate. Such a situation has been observed for the β-silylalcohols **6** and **7**, although in this case a mixture of isomers was still obtained [10].

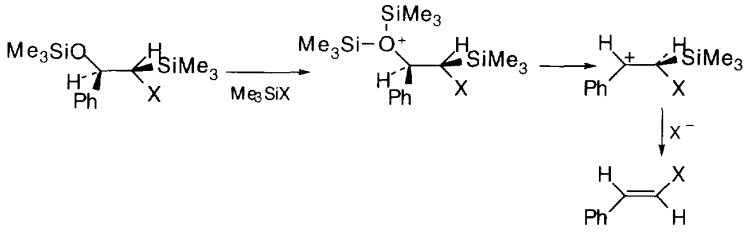
A more likely explanation is that the intermediate **4** or **5** reacts further with the trimethylsilyl halide and undergoes an E1-type elimination. Free rotation about the C-C bond of the carbocation prior to loss of the trimethylsilyl group would lead to the more stable alkene. Carbocation formation is favoured by the adjacent phenyl group.



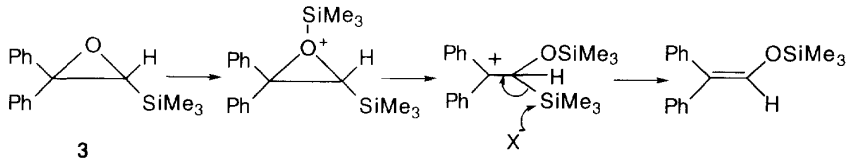
Scheme 4

Addition of trimethylsilyl halides to the α,β-epoxysilane **3** led to the corresponding silyl enol ether in stoichiometric amounts. In this case the presence of the two phenyl groups leads to an S_N1 type ring opening followed by loss of the trimethylsilyl group rather than addition of the nucleophile. This is reminiscent of electrophilic addition to vinylsilanes [11] and the rearrangement of silylepoxides in the presence of boron trifluoride etherate [12]. The rearrangement of **3** was shown to be catalytic in trimethylsilyl halide. Clearly, within the series **1**, **2** and **3**, changing the structure of the substrate has a marked effect on the outcome of the electrophilic addition, revealing that whilst attack α to the silicon is often observed, the directing effect of the silicon can be overcome by electronic effects elsewhere in the epoxide.

Addition of trimethylsilyl azide to the α,β-epoxysilanes **1-3** gave similar products to the trimethylsilyl halides although the yields were often lower. Unlike the trimethylsilyl halides, however, addition to **1** was stereospecific leading to the expected 3:1 *Z*/*E* mixture of alkenes. It is not clear why the stereospecificity of the breakdown of intermediates of the type **4** and **5** to the alkene should depend upon the nature of the halide or pseudohalide attached α to the silicon.



Scheme 5



Scheme 6

Addition of trimethylsilyl cyanide gave the expected products with **2** and **3** albeit in reduced yield. However, reaction of trimethylsilyl cyanide with **1** gave the intermediate adducts **4** and **5**. In all cases attack of the cyanide took place α to the silicon. Such adducts have been observed with conventional epoxides that do not contain a silicon substituent [8, 9], but this is the first report of the production of an α,β-unsaturated nitrile from an α,β-epoxysilane. In the series **1, 2** and **3** each substrate leads to a different product with trimethylsilyl cyanide. Whilst the different products from **2** and **3** can be explained, it is not clear why **1** should stop at the adduct stage whilst **2** goes further to give the alkene product.

Experimental section

NMR spectra were recorded as solutions in deuterated chloroform with tetramethylsilane as internal standard on a Perkin Elmer R12B and a Jeol FX 9OQ spectrometer. Infrared spectra were obtained neat or as nujol mulls or as KBr discs using a Pye Unicam SP 1050 spectrometer. Mass spectra were run on a Cresta MS 30 spectrometer.

Gas chromatograms were obtained on a Pye Unicam Series 204 Chromatograph with a column of 10% SE30 Silicone and 5% Apiezon L (ratio 7:1) on diatamite CAW 100-120 mesh. Column length 2.1 m, internal diameter 4 mm, carrier gas (N_2), flow rate 25 mL/min, splitter 10 @ 18 psi, injector temperature 300°C, detector FID and chart speed 5 mm/min.

Full characterization data are given for new compounds. For known compounds identifications were made by comparison with authentic samples and indicative data only are given below.

Preparation of α,β-epoxysilanes

These were prepared by the method of Magnus and coworkers [13]. Thus *Z*- and *E*-*3-phenyl-2-trimethylsilyloxirane* was obtained as a liquid, bp 37°C/0.16 mmHg; $\delta_H(CDCl_3)$: (*Z*-isomer) −0.18 (s, 9H), 2.48 (d, 1H, J_{cis} = 5.3 Hz), 4.21 (d, 1H, J_{cis} = 5.3 Hz), 7.27 (s, 5H); (*E*-isomer) 0.11 (s, 9H), 2.30 (d, 1H, J_{trans} = 3.3 Hz), 3.65 (d, 1H, J_{trans} = 3.3 Hz), 7.27 (s, 5H); GLC showed the mixture of isomers comprising 22% *Z*-epoxide and 78% *E*-epoxide; *2-trimethylsilyl-1-oxaspiro[2.5]octane* was obtained as a liquid, bp 50-52°C/0.8 mmHg; $\delta_H(CDCl_3)$ 0.08 (s, 9H), 1.48 (s, 10H(broad)), 1.96 (s, 1H); *1,1-diphenyl-2-trimethylsilyloxirane* was obtained as a liquid, bp 32-34°C/0.3 mmHg; $\delta_H(CDCl_3)$ −0.18 (s, 9H), 1.74 (s, 1H), 7.12-7.82 (m, 10H).

The reaction between 3-phenyl-2-trimethylsilyloxirane and trimethylsilyl halides or pseudohalides

Trimethylsilyl iodide. Trimethylsilyl iodide (0.21 g, 1.04 mmol) was added dropwise from a syringe to a solution of *Z* and *E*-3-phenyl-2-trimethylsilyl oxirane (0.20 g, 1.04 mmol) in deuterated chloroform (0.5 mL) under nitrogen. The solution was shaken vigorously and after 1 min, the solution afforded *E*-2-iodophenylethene. GLC showed the presence of one major component. The product was confirmed by comparison of its spectrum with that of an authentic sample [14]. *Trimethylsilyl bromide.* The reaction was carried out as before using trimethylsilyl bromide (1.60 g, 1.04 mmol) and a mixture of *Z* and *E*-3-phenyl-2-trimethylsilyloxirane (0.20 g, 1.04 mmol). After 3 min, the reaction mixture afforded *E*-2-bromo-1-phenylethene. GLC showed only one major component. The product was confirmed by comparison of its spectrum with that of an authentic sample [15]. *Trimethylsilyl chloride.* The reaction was carried out as before using trimethylsilyl chloride (0.02 g, 0.21 mmol) and a mixture of *Z* and *E*-3-phenyl-2-trimethylsilyloxirane (0.04 g, 0.21 mmol). After 2 h, the reaction mixture afforded *E*-2-chloro-1-phenylethene. GLC showed only one major component. The product was confirmed by comparison of the spectrum with that of an authentic sample [16]. *Trimethylsilyl azide.* A solution of *Z*- and *E*-3-phenyl-2-trimethylsilyloxirane (0.31 g, 1.61 mmol) in dichloromethane (2 mL) was added to a solution of trimethylsilyl azide (0.28 g, 2.41 mmol) and zinc chloride (0.03 g, 0.22 mmol) in dichloromethane (7 mL) under nitrogen. The reaction mixture was allowed to stir at room temperature under nitrogen (1 h) and was then heated under reflux at 40°C (5 h). The orange-yellow solution was filtered. The clear reaction mixture was concentrated to dryness to afford a mixture of *Z*- and *E*-2-azido-1-phenylethene;

$\delta_H(CDCl_3)$ 5.05, 5.25 (2d, $2H_Z$, J_{cis} = 6 Hz), 6.11, 6.32 (2d, $2H_E$, J_{trans} = 14 Hz), 7.00-7.60 (m, 5H, Ph).

The product was confirmed by comparison of its spectrum with that of an authentic sample [17].

Trimethylsilyl cyanide. A solution of *Z*- and *E*-3-phenyl-2-trimethylsilyloxirane (0.64 g, 3.34 mmol) in dichloromethane (0.5 mL) was added dropwise from a syringe to a solution containing trimethylsilyl cyanide (0.259 g, 4.48 mmol) and aluminium chloride (0.069 g, 0.45 mmol) in dichloromethane (1 mL). The yellow reaction mixture was allowed to stir at room temperature under nitrogen (1 h) and was then heated under reflux at 40°C (1 h). The cooled reaction mixture was filtered and the clear yellow solution was concentrated to dryness to afford a thick brown-yellow liquid. The major product was (1-cyano-1-trimethylsilyl-2-trimethylsiloxy)phenylethane;

Found : C, 61.6; H, 8.7; N, 5.0%. $C_{15}H_{25}NOSi_2$ requires C, 61.8; H, 8.6; N, 4.8%.

ν_{max} (thin film) 3 090, 3 030, 2 960, 2 900, 2 220, 1 600, 1 500, 1 120, 1 050, 930, 700 cm^{-1}.

δ_H ($CDCl_3$) 0.00 (s, 9H, $SiMe_3$), 0.10 (s, 9H, $OSiMe_3$), 2.20 (d, 1H, J = 5.6 Hz, $CHSiMe_3$), 4.87 (d, 1H, J = 5.6 Hz, CHPh), 7.35 (s, 5H, Ph); δ_C ($CDCl_3$) −2.59 ($SiMe_3$), 0.06 ($OSiMe_3$), 32.11 ($CHSiMe_3$), 72.84 (CHPh), 126.09, 127.01, 128.33, 142.64 (C_6H_5).

The reaction of 2-trimethylsilyl-1-oxaspiro[2.5]octane with trimethylsilyl halides or pseudohalides

Trimethylsilyl iodide. The reaction was carried out as before using trimethylsilyl iodide (0.05 g, 0.36 mmol) and 2-trimethylsilyl-1-oxaspiro[2.5]octane (0.07 g, 0.36 mmol). After 12 h, the reaction afforded iodomethylenecyclohexane;

δ_H ($CDCl_3$) 0.60-2.00 (m, 6H, cyclohexyl Hs), 2.28 (m, 4H, $(CH_2)_2C$=), 5.75 (s, 1H, =CH);

δ_C ($CDCl_3$) 25.28, 26.42, 33.43 (C_6H_{10}), 66.65 (=CH), 118.3 ($C1/C_6H_{10}$).

The product was confirmed by comparison of the ^1H NMR spectrum with that of an authentic sample [18].

Trimethylsilyl bromide. The reaction was carried out as before using trimethylsilyl bromide (0.17 g, 1.09 mmol) and 2-trimethylsilyl-1-oxaspiro[2.5]octane (0.20 g, 1.09 mmol). After 18 h, the reaction afforded bromomethylenecyclohexane;

δ_H ($CDCl_3$) 1.00-2.20 (m, 6H, cyclohexyl Hs), 2.27 (m, 4H, CH_2C=), 5.86 (s, 1H, =CH);

δ_C ($CDCl_3$) 26.13, 27.80, 31.02, 35.50 (C_6H_{10}), 97.54 (=CH), 127.99 ($C1/C_6H_{10}$).

The product was confirmed by comparison of the ^1H NMR spectrum with that of an authentic sample [19].

Trimethylsilyl chloride. The reaction was carried out as before using trimethylsilyl chloride (0.12 g, 1.09 mmol) and 2-trimethylsilyl-1-oxaspiro[2.5]octane (0.20 g, 1.09 mmol). After 20 h, the reaction afforded chloromethylenecyclohexane;

δ_H ($CDCl_3$) 0.70-3.00 (m, 10H, cyclohexyl Hs), 5.75 (s, 1H, =CH);

δ_C ($CDCl_3$) 26.60, 27.80, 34.07 (C_6H_{10}), 108.34 (=CH), 142.01($C1/C_6H_{10}$).

The product was confirmed by comparison of the ^1H NMR spectrum with that of an authentic sample [20].

Trimethylsilyl azide. The reaction was carried out using 2-trimethylsilyl-1-oxaspiro[2.5]octane (0.30 g, 1.63 mmol), trimethylsilyl azide (0.28 g, 2.44 mmol) and zinc chloride (0.03 g, 0.22 mmol) in dichloromethane (12 mL). An orange-yellow solution was obtained after heating under reflux (1 h). On work-up, an orange-yellow liquid was obtained. ^1H NMR showed formation of azidomethylenecyclohexane (45.7%);

δ_H ($CDCl_3$) 1.53-2.09 (m, 10H, cyclohexyl Hs), 5.86 (s, 1H, =CH);

δ_C ($CDCl_3$) 25.57-30.79 (C_6H_{10}), 122.71 ($C1/C_6H_{10}$) 130.29 (=CH).

The product was confirmed by comparison of the ^1H NMR spectrum with that of an authentic sample [21].

Trimethylsilyl cyanide. The reaction was carried out as before using trimethylsilyl cyanide (0.18 g, 1.79 mmol), 2-trimethylsilyl-1-oxaspiro[2.5]octane (0.30 g, 1.63 mmol) and aluminium chloride (0.07 g, 0.52 mmol). After 30 min, on work-up, the reaction afforded cyanomethylenecyclohexane;

δ_H ($CDCl_3$) 1.48-2.68 (m, 10H, cyclohexyl Hs), 5.06 (m, 1H, =CH).

The product was confirmed by comparison of the ^1H NMR spectrum with that of an authentic sample [22].

The reaction of 2,2-diphenyl-3-trimethylsilyloxirane with trimethylsilyl halides in catalytic quantities

Trimethylsilyl iodide. The reaction was carried out as before using trimethylsilyl iodide (0.007 g, 0.03 mmol) and 2,2-diphenyl-3-trimethylsilyloxirane (0.18 g, 0.68 mmol). After 2 min, the reaction afforded a reddish brown liquid containing 1,1-diphenyl-2-trimethylsiloxyethene;

Found : C, 76.1; H, 7.3; N, 5.9%. $C_{17}H_{20}OSi$ requires C, 76.1; H, 7.5; N, 6.0%. ν_{max} (neat) 3 100-3 020, 2 960, 2 900, 1 625, 1 600, 1 523, 1 475, 1 443, 1 250, 1 215, 1 119, 1 072, 1 030, 955, 910, 850, 765, 700 cm^{-1};

δ_H ($CDCl_3$) 0.40 (s, 9H, $SiMe_3$), 6.90 (s, 1H, =CH), 7.50 (s, 10H, Ph);

δ_C ($CDCl_3$) 0.46 ($SiMe_3$), 128.16, 128.62, 128.97, 130.34 (C_6H_5), 138.68 ($CHOSiMe_3$), 141.26 (=CPh_2).

Trimethylsilyl iodide was recovered in a quantitative amount.

Trimethylsilyl bromide. The reaction was carried out using trimethylsilyl bromide (0.005 g, 0.04 mmol) and 2,2-diphenyl-3-trimethylsilyloxirane (0.19 g, 0.70 mmol). After 10 min, the reaction afforded 1,1-diphenyl-2-trimethylsiloxyethene. The product was confirmed by comparison of spectra with that of the authentic sample given above. Trimethylsilyl bromide was recovered in a quantitative amount.

Trimethylsilyl chloride. The reaction was carried out using trimethylsilyl chloride (0.004 g, 0.04 mmol) and 2,2-diphenyl-3-trimethylsilyloxirane (0.19 g, 0.71 mmol). After 2 h, the yellow solution afforded 1,1-diphenyl-2-trimethylsiloxyethene. The product was confirmed by comparison of spectra with that of the authentic sample given above. Trimethylsilyl chloride was recovered in a quantitative amount.

Trimethylsilyl azide. The reaction was carried out using 2,2-diphenyl-3-trimethylsilyloxirane (0.409 g, 1.49 mmol), trimethylsilyl azide (0.26 g, 0.22 mmol), zinc chloride (0.039 g, 0.22 mmol) in dichloromethane (12 mL). The reaction mixture was heated under reflux at 40°C (1 h). On work-up, the reaction afforded 1,1-diphenyl-2-trimethylsiloxyethene. The product was confirmed by comparison of spectra with that of the authentic sample given above.

Trimethylsilyl cyanide. The reaction was carried out using 2,2-diphenyl-3-trimethylsilyloxirane (0.60 g, 2.24 mmol), trimethylsilyl cyanide (0.24 g, 2.46 mmol) and zinc chloride (0.34 g, 2.46 mmol) in dichloromethane (12 mL). On work-up, the reaction afforded 1,1-diphenyl-2-trimethylsiloxyethene. The product was confirmed by comparison of spectra with that of an authentic sample given above. Trimethylsilyl cyanide was recovered in a quantitative amount.

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