Directive and Shielding Effects of the Trimethylsilyl Group. Unprecedented β-Selectivity in the Reaction of α,β-Epoxyalkylsilanes with Hindered α-Sulphonyl Anions

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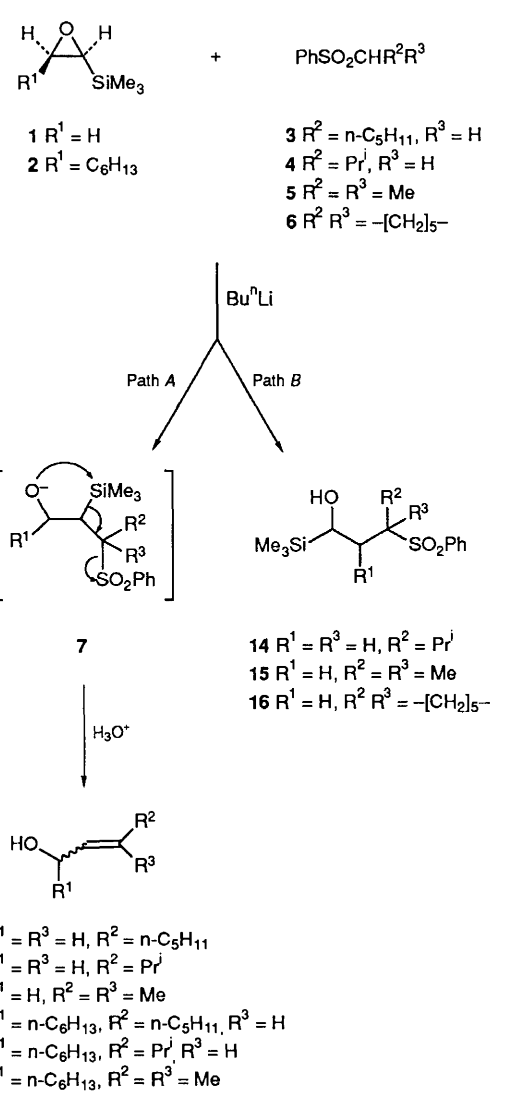
Anions generated from hindered primary and secondary alkyl phenyl sulphones react with trimethylsilyloxirane to yield a mixture of products of addition in α- and β-positions or exclusively the product of addition in the β-position.

It is well documented that the reaction of (α,β-epoxyalkyl)-silanes with many nucleophiles occurs regioselectively with addition of the nucelophile at the α-position.[1] No exception to the α-attack rule had been recorded† (to the best of our knowledge) until Schaumann and Kirsching[3] recently reported that the reaction of lithiated allylsilanes with some (α,β-epoxyalkyl)silanes affords the products of addition in the α-position, accompanied by various amounts (up to 25%) of the corresponding regioisomers. This communication prompted us to disclose our observations regarding the relative strength of the directive effect exerted by silicon, as compared to the shielding effect[4] of the trimethylsilyl group in α,β-epoxyalkylsilanes.



Scheme 1

Trimethylsilyloxirane[5] **1** (Scheme 1) was treated in tetrahydrofuran (THF) [at −20 °C, slowly increasing to room temperature during 16 h] with anions generated from the primary and secondary phenyl sulphones **3–6** and n-butyllithium. The results are presented in Table 1.

The reaction of **1** with lithiated n-hexyl phenyl sulphone **3** yielded the allylic alcohol **8** as the only product (Table 1, entry 1). This product is formed *via* adduct **7** and the *O*-trimethylsilyl derivative of alcohol **8** (path *A*, Scheme 1)[6] and reflects the attack of the nucleophile in the α-position. The sulphone **4** with a β-branched alkyl chain afforded allylic alcohol **9** and silylcarbinol **14**, which are products of α- and β-attack (paths *A* and *B*, respectively) (entry 2). With isopropylphenyl sulphone **5** the product of β-attack **15** predominated (entry 3) and in the case of cyclohexyl phenyl sulphone **6** the silylcarbinol **16** was the exclusive product (entry 4).

Reactions of *cis*-1-octyl-2-trimethylsilyloxirane **2** with anions generated from the sulphones **3–6**, under analogous conditions, were next examined. Sulphone **3** yielded allylic alcohol **11** (Table 1, entry 5). The reaction involving isobutyl sulphone **4** was sluggish; it afforded, however, exclusively the product resulting from α-attack **12** (entry 6). Finally, the reaction of isopropyl sulphone **5** gave the allylic alcohol **13** (in rather high yield) whereas the very hindered anion generated from cyclohexyl sulphone **6** failed to react with the oxirane **2**. The product of nucleophilic attack on the β-position of the α,β-epoxyalkylsilane **2** (route *B*) was not detected in any reaction.

The α-regioselectivity in the reactions of α,β-epoxyalkylsilanes with nucleophiles (*e.g.* in reduction with lithium aluminium hydride,[7] and in addition of lithium cuprates)[8] is opposite to that expected on the grounds of the steric effects prevailing in the reactions of all-carbon epoxides since the substituent in the α-position (the trimethylsilyl group) is more bulky than that in the β-position (hydrogen or alkyl group). The directive effect exerted by the silicon-containing substituent has been explained (*i*) in terms of interaction of the nucleophile with the vacant 3d orbital of the silicon atom,[7,9] or (*ii*) in terms of the antibonding interaction between the oxygen 2p and C–Si σ-orbitals which activate the α-carbon atom.[10]

Table 1 Reaction of lithiated sulphones with (α,β-epoxyalkyl)-trimethylsilanes **1** or **2** (Scheme 1)

			Products (% yield)[a]	
Entry	Epoxide	Sulphone	Path *A*	Path *B*
1	**1**	**3**	**8**(57)[b]	—
2	**1**	**4**	**9**(35)[c]	**14**(40)
3	**1**	**5**	**10**(31)	**15**(45)
4	**1**	**6**	—	**16**(73)
5	**2**	**3**	**11**(80)[d]	—
6	**2**	**4**	**12**(14)[e]	—
7	**2**	**5**	**13**(57)	—

[a] Isolated yields. [b] (*E*)- and (*Z*)-Isomers in a 1 : 15 ratio. [c] (*E*) : (*Z*) = *ca.* 3 : 1. [d] (*E*) : (*Z*) = 1 : 11. [e] (*E*) : (*Z*) = *ca.* 2 : 1.

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† In the reaction of 1-propyl-1-trimethylsilyloxirane with propylmagnesium bromide, 4-hydroxy-4-trimethylsilyloctane was formed as a minor product,[2] probably by oxirane opening in the β-position.

Our experiments seem to favour the latter explanation, as simultaneous interaction of the sulphonyl anion with silicon and carbon atoms is unlikely owing to the bulk of the phenylsulphonyl group, even if the alkyl group of the sulphone is small. The bulk of the alkyl group of the sulphone is, however, of importance. With an increase in the bulk of the alkyl group, the directive effect of the silicon atom is hampered by repulsion between the nucleophile and the large trimethylsilyl group. The reaction of the oxirane **1** with very bulky sulphonyl anions affords partly or selectively the product of addition in the unhindered β-position (the shielding effect is of the same order or it dominates over the directive effect). We conclude that the regioselectivity in nucleophilic opening of the oxirane ring in α,β-epoxyalkyltrimethylsilanes is determined by the α-directive effect of silicon as well as by the shielding effect of the trimethylsilyl group (and of other substituents) on the oxirane ring.

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