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The reaction of trimethylsilyl ethylene oxide with α-sulfonyl anions and α,α-sulfonyl dianions. A method for stereocontrolled synthesis of (*E*)- and (*Z*)-allylic alcohols

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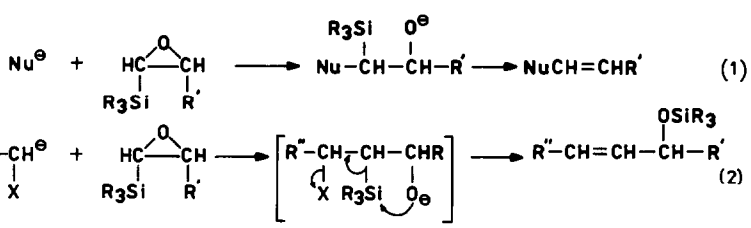
Abstract

Trimethylsilyl ethylene oxide has been shown to react with α-sulfonyl carbanions generated from representative primary alkyl phenyl sulfones to give the corresponding O-trimethylsilyl allylic alcohols, with higher selectivity for (*Z*)-isomers. The reaction proceeds by attachment of the nucleophile to the α-position of the α,β-epoxyalkylsilane followed by a carbon-to-oxygen shift of the trimethylsilyl group and expulsion of the benzenosulfonyl anion. The reaction of trimethylsilyl ethylene oxide with α,α-sulfonyl dianions followed by partial protonation of the immediate adducts affords O-trimethylsilyl allylic alcohols, mainly (*E*)-isomers. The reaction of trimethylsilyl ethylene oxide with α-sulfonyl carbanions generated from secondary alkyl phenyl sulfones affords α-trimethylsilyl carbinols as the only or predominant product. In this case the attachment of the nucleophile takes place at the β-position of the α,β-epoxyalkylsiane. The origin of the regio- and stereo-selectivity in reactions of sulfonyl carbanions with α,β-epoxyalkylsilanes is discussed.

Introduction

(α,β-Epoxyalkyl)trialkylsilanes are useful intermediates in stereocontrolled synthesis of alkenes (Hudrlik–Peterson olefination) and alkenes substituted in the vinylic position by a variety of atoms and functional groups, e.g. enol ethers, enamines and vinyl stannanes [1,2]. In these applications the epoxyalkylsilane moiety serves as a masked stereochemically defined ethylene unit in that the attack of an appropriate nucleophile takes place at the α position to yield a β-oxidosilane, which is then undergoes elimination of trialkylsiloxide with formation of a double



(1)

(2)

bond (Eq. 1). Recently [3] we have found that nucleophiles bearing an appropriate leaving group at the nucleophilic center, such as lithiated alkyl aryl sulfones, react

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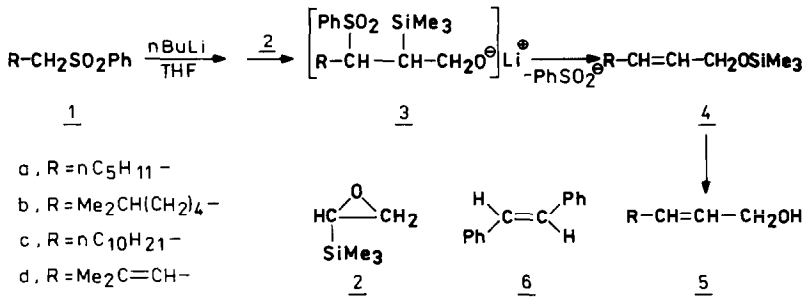


Scheme 1.

with α,β-epoxyalkylsilanes in a different way. After addition of nucleophile to the α-carbon atom, a 1,3-shift of the silicon substituent from carbon to oxygen occurs with concomitant expulsion of the leaving group to give a trimethylsilyl ether of allylic alcohol (Eq. 2). When the nucleophile is an anion derived from primary alkyl phenyl sulfone (Eq. 2, X + SO_2Ph), the product consists mainly of the allylic alcohol isomer with the (Z) configuration of the double bond (the epoxysilane serves as a stereochemically defined =CHCH(OH)R unit). To provide a better understanding of this reaction, which may be used for preparative synthesis of allylic [4] and possibly other unsaturated alcohols, we undertook study of reactions of a range of epoxyalkylsilanes and nucleophiles bearing a leaving group at the electron-donating center. We present below the results for the reaction of trimethylsilyl ethylene oxide (**2**) with mono- and di-anions generated from selected alkyl phenyl sulphones [5]. We also describe some transformations of the immediate reaction products, and discuss the origin of the regio- and stereo-selectivity in the reaction of α-β-epoxyalkylsilanes with sulphones.

Results and discussion

Reactions of α-sulfonyl monoanions

Trimethylsilyl ethylene oxide (**2**) (Scheme 1) [6] in tetrahydrofuran (THF) was treated at −20 °C with lithiated phenyl undecyl sulfone prepared from **1c** (1.5 molar equivalents) and n-butyllithium (1.4 molar equivalents). A precipitate ($PhSO_2Li$) was gradually, and the reaction was complete within ca. 16 h. At first, the initial reaction product silyl ether **4c** was isolated. As silyl ethers are partly hydrolyzed during aqueous work-up and during chromatography on silica gel, in later work the crude product was hydrolyzed with methanol containing a trace of perchloric or *p*-toluenesulphonic acid (*p*-TSA) to give the free alcohol, which could be handled without difficulty. By use of the latter procedure, tridec-3-en-1-ols **5c** were obtained in a 69% yield as a mixture of (E) and (Z) isomers in a 1 : 11 ratio. Likewise, the reaction of epoxide **2** with lithiated primary sulphones **1a** and **1b** afforded the primary allylic alcohols **5a** and **5b**. The yields and isomer ratios are shown in Table 1. The reaction of phenyl prenyl sulfone (**1d**) with oxirane **2** afforded hydroxy diene **5d** in 57% yield as a mixture of isomers (Table 1). Under analogous conditions benzyl phenyl sulfone (**1e**) gave cinnamyl alcohols (**5e**) in low yield. Unexpectedly, *trans*-stilbene (**6**) was the major product, isolated in a 42% yield. Presumably compound **6** results from substitution of the benzenesulfonyl

Table 1

The reaction of trimethylsilyl ethylene oxide (**2**) with lithium derivatives of primary alkyl phenyl sulfones

Entry	Sulfone	Product	Yield(%)	*E*: *Z* ratio
1	**1a**	**5a**	57	1:15
2	**1b**	**5b**	65	1:13 [a]
3	**1c**	**5c**	69	1:11
4	**1d**	**5d**	57	1:5
5	**1e**	**5e**	– [b]	
6	**1e**	**5e**	76 [c]	1:0.83

[a] Ref. 4. [b] Estimated at 10%; *trans*-stilbene was the major product. [c] Excess of oxirane was used.

group in the sulfone (used in excess) by lithiated sulfone *. This side reaction was suppressed, however, when an excess of oxirane was used (Table 1, Entry 6); the lower selectivity towards the reaction of sulfone **1e** and the predominance of the (*E*) isomer of the product are noteworthy.

Comments on the stereoselectivity of the reaction

The reactions of primary alkyl sulfones (**1a**, **1b**, and **1c**) with oxirane **2** yielded allylic alcohols, with marked selectivity towards the isomers with (*Z*) configuration of the double bond. It seemed reasonable to assume that in the intermediate adducts **3** migrations of the trimethylsilyl group and elimination of the benzenesulfonic group take place in a concerted manner. To comply with the general stereoelectronic requirements such a process requires a conformation with *anti*-periplanar alignment of the C–Si and C–S bonds. As a consequence, the ratio of double-bond isomers in the product reflects the ratio of diastereomers in the intermediate adduct **3**. The ratio of diastereomers depends, in turn, upon "asymmetric induction" during the formation of the chiral center at the carbon earing the $PhSO_2$ group.

The stereochemical consequences of addition of carbanions generated from prochiral sulfones ** or similar species to chiral oxiranes have not so far, to our best knowledge, been investigated. Recently Bassindale et al. [9] have, however, proposed a stereochemical model for the kinetically controlled reaction of prochiral carbanions with prochiral carbonyl compounds. In this model a reactant-like transition state is assumed and the steric course of the reaction is predicted from the early interactions between the reactants. Comparison of nucleophilic additions to carbonyl and oxirane carbon atoms indicates that the major difference between them involves the angle of the approach of the nucleophile to the reaction center. Whereas the carbonyl moiety is essentially flat and the attack of the nucleophile occurs at an angle of ca. 109° to the plane on which atoms of the carbonyl group and vicinal atoms are situated [10], electrophilic carbon of the oxirane is tetrahedral. The addition of nucleophile to a tetrahedral carbon should, in principle, take place along the line of the C–O bond and involve a bipyramidal arrangement of substituents around the central carbon atom [10,11]. Taking into account the distortion of angles in the oxirane ring, we assume, however, that nucleophilic attack on the oxirane occurs at an angle close to 109° relative to the oxirane C–C bond

* The reaction of two molecules of lithiated sulfone, like the recently described [7] reaction of α-sulfonyl carbanions with halogenolithiocarbenes, represents a plausible alternative.

** For a discussion on the structure of α-sulfonyl carbanions, see Ref. 8.

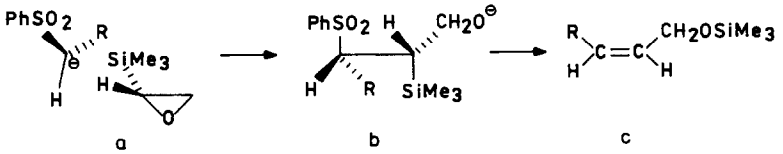


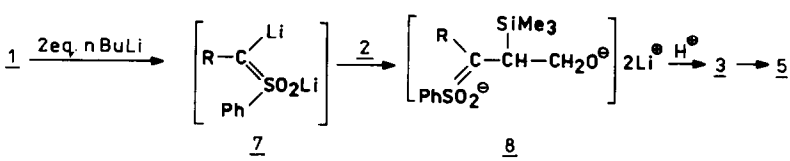
Fig. 1.

(Fig. 1). On this assumption, we have analyzed the extension of the Bassindale model for the addition of sulfone to α,β-epoxyalkylsilanes. According to this model, the following two factors are decisive for this reaction. (1) The major contribution to the non-bonding interactions in the transition state arises from the proximity between one of the nucleophiles substituent and two substituents on the oxirane carbon atom; for this reason the smallest substituent (H) of the nucleophile would be located in this position (Fig. 1, a). (2) In the favored transition state, the largest group on the nucleophile ($PhSO_2$) is thus located in the proximity of the oxirane proton whereas the medium group (R) is situated on the side of the trimethylsilyl group (Fig. 1, a). In terms of such a model, the *syn* (*erythro*, less stable) isomer of the adduct is dominant (Fig. 1, b), and consequently the product with (*Z*) configuration of the double bond would be formed in excess. In conclusion, this model explains the above-presented and other [3] results for the reaction of lithiated alkyl phenyl sulfones with α,β-epoxyalkylsilanes. The low selectivity in the reaction of phenyl benzyl sulfones with oxirane **2** (Table 1, Entry 6) reflects the relatively smaller difference in bulk between the phenyl and phenylsulfonyl groups then between the alkyl and phenylsulfonyl substituents.

Reactions of α,α-sulfonyl dianions

In a search for a stereochemical alternative to the process described above we examined the reaction of sulfone dianions [12,13] with epoxide (**2**). It was expected that after addition of the dianion **7** to oxirane **2** (Scheme 2) and partial protonation of the adduct **8**, migration of the silicon substituent and elimination of the benzenesulfonyl group would occur to give the O-trimethylsilyl allylic alcohol, as in the case of the monoanion. The ratio of the intermediate diasteromeric adducts **3** would, however, be determined by the steric course of protonation.

Treatment of sulfone **1a** in THF at 0 °C with 2 molar equivalents of n-butyllihtium afforded the dianion *, which was allowed to react with oxirane **2** and the reaction mixture then treated (at −78 °C) with one molar equivalent of *p*-nitro-



Scheme 2.

* Quenching of the dianion with D_2O gave deuterated sulfone, which was shown from its ^1H NMR spectrum to be at least 80% deuterated in the α-positions.

Table 2

The reaction of trimethylsilyl ethylene oxide (2) with dilithium derivatives of primary alkyl phenyl sulfones

Sulfone	n-BuLi [a]	2 [a]	Proton source	Product		
				yield	(%)	$E:Z$ ratio
1a	2	0.75	p-NO_2-C_6H_4COOH	**5a**	59	7.0:1(1:15) [b]
1a	2	0.7	t-BuOH	**5a**	59	2.3:1
1a	2	0.75	hept-1-yne	**5a**	61	5.6:1
1d	2	0.7	p-NO_2-C_6H_4COOH	**5d**	48	1.2:1(1:5)

[a] Molar equivalents. [b] Product ratios in the reactions of the corresponding mono-anions are given in brackets.

benzoic acid *. Isolation of product after benzoylation gave the benzoates of the allylic alcohols **5a** in a 59% yield. In contrast to the outcome of the reaction of the corresponding monoanion, the (E) isomer predominated (Table 2). Under similar conditions phenyl prenyl sulfone (**1d**) gave dienyl alcohols **5d**, again with a different ratio of isomers (Table 2).

The use of p-nitrobenzoic acid for protonation of the dianion requires some comment. It has recently been shown by Trost and Merlic [12] that the stereochemistry of the reaction of dianion of allylic sulfones with monosubstituted all-carbon oxiranes is governed by the protonation step, which yields the kinetic or thermodynamic products depending upon the conditions. In the present work no attempt was made to determine the relative rates of protonation and of the subsequent steps in the reaction illustrated in Scheme 2, but it seemed interesting to seek insight into the role of the proton source. For this reason the additional reactions of the dianion of sulfone **1a** with oxirane **2** were carried out with t-butanol or 1-heptyne (cf. Ref. 14) for protonation of the adduct. Under these conditions the ratio of the double-bond isomers was markedly different (see Table 2).

The results for the above-described reactions of sulfone anions and dianions indicate that the ratio of geometric isomers of the products is critically dependent upon the amount of n-butyllithium used to generate the anion. This point is illustrated by the data shown in Table 3.

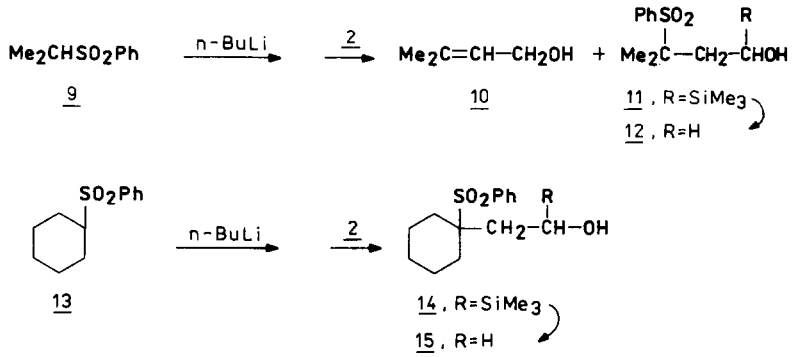
Table 3

The effect of the amount of n-butyllithium used to generate the anions on the stereochemistry of the reaction [a]

Sulfone **1a** (mmol)	n-BuLi (mmol)	**2** (mmol)	Product **5a**	
			Yield(%) [b]	$E:Z$ ratio
8.84(1.31)	8.00(1.18)	6.76(1)	57	1.0:15
3.98(1.29)	7.96(2.15)	3.07(1)	61	5.6:1 [c]
8.84(1.20)	12.4(1.75)	7.07(1)	69	1.0:1.3 [c]

[a] Molar equivalents relative to epoxysilane are given in brackets. [b] Based on epoxysilane. [c] Reactions were quenched with t-BuOH at 0 °C.

* The amount of acid was calculated in such a way that excess of the starting dilithium sulfone would also be protonated.



Scheme 3.

Reactions involving secondary alkyl phenyl sulfones

The reaction of epoxide **2** with lithiated isopropyl phenyl sulfone (**9**) (Scheme 3), followed by mild acid hydrolysis, gives a mixture of two products, one of which was readily identified as 3-methyl-but-2-en-1-ol (**10**). Since this compound is relatively volatile, the crude mixture was benzoylated in the usual way and the product chromatographed on silica gel. Three compounds were separated, and identified as follows: (1) the benzoate of allylic alcohol **10** (31% yield); (2) the α-trimethylsilyl carbinol **11** (34%); and (3) the benzoyl-derivative of this carbinol (11%). Obviously the sterically hindered carbinol **11** was only partly benzoylated under the conditions used. It was concluded that the reaction of sulfone **9** with epoxide **2** gave the product of attack on the α- (**10**) and β-positions (**11**) in a 41 : 59 ratio (total yield 76%).

The structure of compound **11** followed from its elemental composition and spectra (see Experimental Section). To confirm this assignment of structure, alcohol **11** was treated with 3 molar equivalents of sodium hydride in ether in the presence of hexamethylphosphoramide (HMPA) under conditions of the Brook rearrangement [15,16]. The O-silylated alcohol **12** was obtained *. A higher yield of the rearranged product was obtained when carbinol **11** was treated with a large excess of sodium hydride in ether.

The reaction of trimethylsilyl ethylene oxide (**2**) with lithiated cyclohexyl phenyl sulfone (**13**) afforded a single product. Its ^{1}H NMR spectrum was consistent with the structure generated by nucleophile attack at the β-position of the epoxysilane **2**. To confirm this structure, the product was protiodesilylated with tetrabutylammonium fluoride in methanol, to give hydroxylsulfone **15** in 80% yield.

Comments on regioselectivity of reactions of α,β-epoxyalkylsilanes

The regioselectivity of nucleophilic additions to α,β-epoxyalkylsilanes has attracted considerable attention, as whatever the steric and electronic effects, all the reactions previously reported involved attack exclusively at the α-position. This mode of reaction, initially observed in the study of the reaction of α,β-epoxyalkylsilanes with lithium aluminum hydride, has been attributed to simultaneous

* Our attempts to combine the Brook rearrangement with expulsion of the phenylsulfonyl group and closure of the cyclopropane ring here so far been unsuccessful (cf. Ref. 17).

interaction of the approaching electron pair with the antibonding orbital of the epoxide carbon and with the vacant 3d orbital of silicon [19], in keeping with the explanation but forward for nucleophilic displacement in α-silyl halides [20]. In many other instances the interaction of nucleophile with silicon has been used to account for the mode of reaction of organosilicon compounds; for some of these reactions compelling evidence for the participation of an intermediate with a 5-coordinated silicon was obtained [21]. In all such cases, however, small and hard nucleophiles were involed in the interaction with the silicon atom. On the other hand, Paquette, Gleiter et al. [22] have postulated that the regioselectivity in the reactions of α,β-epoxyalkylsilanes is due to antibonding interactions between the oxygen $2p$ and C–Si σ-orbitals, which raises their HOMO level [23]; these authors have emphasized that the C–Si and C–O bonds are arranged in a fashion that does not lead to stabilization of the developing charge in the β-position.

The bulk of the phenyl sulfonyl group seems to rule out an initial attack of the sulfonyl anion on the silicon atom. In the light of our results activation of α-position in epoxyalkylsilanes seems to play an important role in the electrophilic reaction of this functional group. However, in the case of anions of secondary alkyl phenyl sulfones, steric repulsion of two particularly bulky groups at the reaction center predominates over the electronic effect *. To the best of our knowledge the above-described reactions represent the first observed instances of nucleophilic attack at the β-position of α,β-epoxysilanes **.

Experimental

General

Melting points were determined on a Kofler hot-stage. The spectra were recorded with the following instruments: IR – Beckmann 4240 or Unicam SP 200 spectrophotometers; NMR – Bruker AM 500 (500 MHz for ^1H and 125 MHz for ^{13}C) spectrometer (in $CDCl_3$). Chemical shifts are reported in δ units, downfield from tetramethylsilane. All reactions involving sulfonyl anions were carried out under argon. THF and ether were dried with lithium aluminum hydride and then with potassium–sodium alloy. Column chromatography was performed on silica gel, Merck, 230–400 mesh unless otherwise stated, and TLC was on silica gel G, Merck. Organic solvents were dried over anhydrous Na_2SO_4 and solvents were removed under reduced pressure with a rotary evaporator. Microanalyses were performed in our Institute.

*Oct-2-ene-1-ols (**5a**)*

1. Reactions involving α-sulfonyl monoanions. To a stirred solution of sulfone **1a** (2.0 g, 8.84 mmol) in THF (20 ml), at $-20\,^\circ C$ was added dropwise n-BuLi in hexane (1.6 *M*, 5.0 ml, 8.0 mmol). Stirring was continued for 15 min and epoxide **2**

* The reaction of lithiated i-propyl phenyl sulfone with (α,β-epoxyoctyl)trimethylsilane gave exclusively the product of α-addition, 2-methyl-dec-2-en-3-ol (57% yield) [24], confirming the dominance of the steric effect on the regioselectivity.

** After completion of this work it has been reported [25] that reaction of allyl silyl anions with **2** affords the product of α-addition accompanied by some product of β-addition.

(0.786 g, 6.76 mmol) in THF (5 ml) was then added during 40 min. After a further 2 h at −20 °C the mixture was allowed to warm to room temperature and set aside overnight. Water (50 ml) was added and the product was extracted with pentane (3 × 50 ml). The extract was concentrated by use of a 15 cm Vigreaux column and the residue (ca. 2 ml) was treated with methanol (20 ml) containing 70% perchloric acid (0.01 ml). After 1 h the mixture was diluted with water (30 ml) and extracted with CH_2Cl_2 (3 × 50 ml). The extract was concentrated using a column and the residue diluted with CH_2Cl_2 (15 ml) containing pyridine (1.6 ml, 20 mmol) and then treated with benzoyl chloride (0.950 g, 6.76 mmol) in CH_2Cl_2 (5 ml). The mixture was stirred at room temperature for 1 h and water (50 ml) then added, and the product extracted with pentane (3 × 50 ml). The pentane solution was successively washed with 10% aq. H_2SO_4 (50 ml), saturated aqueous $NaHCO_3$ (50 ml), and water (3 × 50 ml), and the solvent then evaporated in vacuo. The residue was twice dissolved in hexane and the solution was evaporated in vacuo (to remove THF) and then chromatographed on SiO_2 (50 g, benzene–hexane, 1 : 1) to give the benzoate of **5a** (0.957 g, 57% yield) as a mixture of (*E*) and (*Z*) isomers in a 1 : 15 ratio; δ_H 7.93–7.27 (5H, m, aromat H), 5.60–5.50 (2H, m, C_2- and C_3-H), 4.74 (2H, br d, $J_{1,2}$ = 5.69 Hz, C_1-H), 2.03 (2H, br q, J = 6.8 Hz, C_4-H), 1.30–1.15 (6H, m, C_5-, C_6- and C_7-H), 0.75 (3H, t, J = 7.0 Hz, C_8-H) (isomer *Z*); 7.93–7.27 (5H, m, aromat H), 5.74–5.50 (2H, m, C_2- and C_3-H), 4.63 (2H, dd, $J_{1,2}$ = 6.42, $J_{1,3}$ = 1.03 Hz, C_1-H), 1.93 (2H, m, C_4-H), 1.30–1.15 (6H, m, C_5-, C_6- and C_7-H), 0.75 (3H, t, J = 7.0 Hz, C_8-H) (isomer *E*); on irradiation at 4.74 ppm the multiplet at 5.60–5.50 collapses to a multiplet and to a doublet (δ 5.67) which corresponds to C_2-H, $J_{2,3}$ = 11.2 Hz; δ_C 13.91, 22.43, 27.53, 29.06, 31.33 (C_4–C_8), 60.77 (C_1), 123.3, 135.61 (C_2 and C_3), 128.22, 129.54, 130.38 and 132.74 (C-aromat.), 166.44 (C=O) (isomer *Z*); 13.95, 22.46, 28.53, 31.33, 32.21 (C_4–C_8), 65.68 (C_1), 123.75, 136.62 (C_2 and C_3), 128.24, 129.54, 130.42, 132.57 (C-aromat.), 166.36 (C=O) (isomer *E*).

2. Reactions involving dianions. (1) To a stirred solution of sulfone **1a** (0.905 g, 4 mmol) in THF (17 ml), at 0 °C a solution of n-BuLi in hexane (1.6 *M*, 5.0 ml, 8.0 mmol) was added during 10 min. After a further 30 min the mixture was cooled to −20 °C and a solution of epoxide **2** (0.349 g, 3 mmol) in THF (3 ml) was added during 10 min. The mixture was stirred at −20 °C for 2 h and then at room temperature for 18 h. The clear solution was cooled to −78 °C and treated with a solution of *p*-nitrobenzoic acid (0.836 g, 5 mmol) in THF (8 ml). The cooling was then moderated, and after 1 h, at −50 °C a precipitate started to form. The mixture was allowed to warm to room temperature and stirring was continued for a further 5 h. Water (40 ml) was added and the product extracted with pentane (3 × 30 ml). The extract was concentrated under a fractionating column to ca. 3 ml and the residue diluted with methanol (20 ml) containing a catalytical amount of *p*-TSA monohydrate. The mixture was set aside and after 45 min diluted with water (30 ml) and extracted with CH_2Cl_2 (3 × 30 ml). The extract was washed with aqueous sodium carbonate and dried, and the solvent distilled off under a column. The residue (ca. 3 ml) was diluted with CH_2Cl_2 (20 ml) containing pyridine (4 ml) and treated with benzoyl chloride (0.858 g, 6.0 mmol) in CH_2Cl_2 (5 ml). The mixture was stirred at room temperature for 1 h then water (40 ml) was added and the product extracted with pentane (3 × 30 ml). The pentane solution was washed successively with 5% aqueous H_2SO_4 (50 ml), saturated aqueous $NaHCO_3$ (50 ml), and water (3 × 50 ml), and the solvent evaporated in vacuo. The residue was

chromatographed on SiO_2 (40 g, benzene–hexane, 1 : 2) to give the benzoate of **5a** (0.441 g, 59% yield) as a mixture of (*E*) and (*Z*) isomers in a 7 : 1 ratio.

(2) In an analogous experiment *p*-nitrobenzoic acid was replaced by t-butanol. The reagents were used as follows: sulfone 1a (0.745 g, 3.33 mmol), n-BuLi (1.6 *M* in hexane, 4.2 ml, 6.66 mmol), epoxysilane **2** (0.291 g, 2.5 mmol) and THF (18 ml), and then t-BuOH (0.308 g) in ether (1 ml) (the precipitate started to separate 2 h after addition of t-BuOH, when the temperature reached −5 °C), and finally pyridine (4 ml) and benzoyl chloride (0.703 g, 5 mmol). The benzoates of alcohols **5a** obtained (0.368 g, 59% yield) had the (*E*) and (*Z*) isomers in a 2.3 : 1 ratio.

(3) In an analogous experiment *p*-nitrobenzoic acid was replaced by 1-heptyne. The reagents were used as follows: sulfone 1a (0.745 g, 3.33 mmol), n-BuLi (1.6 *M* in hexane, 4.2 ml, 6.66 mmol), epoxysilane **2** (0.290 g, 2.5 mmol) and THF (18 ml) and then 1-heptyne (0.401 g, 4.17 mmol) (the precipitate started to separate after the mixture has been kept at room temperature for 6 h), and finally pyridine (4 ml) and benzoyl chloride (0.703 g, 5 mmol). The benzoates of alcohols **5a** obtained (0.379 g, 61% yield) had the (*E*) and (*Z*) isomers in a 5.6 : 1 ratio.

*Tridec-2-en-1-ols (**5c**)*

To stirred a solution of sulfone **1c** (2.0 g, 6.75 mmol) in THF (20 ml), at −20 °C was added dropwise n-BuLi in hexane (1.2 *M*, 5.6 ml, 6.72 mmol). Stirring was continued for 15 min and epoxide **2** (0.513 g, 4.42 mmol) in THF (5 ml) then added during 1.5 h. After an additional 2 h, the mixture was allowed to warm to room temperature and was set aside overnight. Water (30 ml) was added and the product extracted with pentane (2 × 70 ml). The extract was concentrated and the residue (ca. 2 ml) diluted with methanol (10 ml) containing 70% perchloric acid (0.01 ml). After 1 h the mixture was diluted with water (20 ml) and extracted with CH_2Cl_2 (3 × 25 ml). The extract was concentrated under a column and the residue (1.7 g) was chromatographed on SiO_2 (85 g, 70–230 mesh, pentane–ether, 6 : 1) to give alcohol **5c** (0.605 g, 69% yield) as a mixture of (*E*) and (*Z*) isomers in a 1 : 11 ratio; ν_{max}(film) 3320 (OH) cm^{-1}; δ_H 5.59 (1H, dtt, $J_{2,3} = 10.7$, $J_{2,1} = 6.5$, $J_{2,4} = 1.1$ Hz, C_2-H), 5.54(1H, dtt, $J_{3,2} = 10.7$, $J_{3,4} = 7.2$, $J_{3,1} = 1.1$ Hz, C_3-H), 4.19 (2H, br d, $J_{1,2} = 6.2$ Hz, C_1-H), 2.07 (2H, br q, $J = 7$ Hz, C_4-H), 1.4–1.2 (16H, m, C_5–C_{12}-H), 0.88 (3H, t, $J = 7.1$ Hz, C_{13}-H) (*Z*-isomer); 5.73–5.63 (2H, m, C_2- and C_3-H), 4.08 (2H, dd, $J_{1,2} = 5.7$, $J_{1,3} = 0.8$ Hz, C_1-H), 2.04 (2H, m, C_4-H), 1.4–1.2 (16H, m, C_5–C_{12}-H), 0.875 (3H, t, $J = 7.1$ Hz, C_{13}-H); δ_C 13.99 (C_{13}), 22.61 and 32.73 (C_4 and C_{12}), 58.44 (C_1), 128.39 and 132.96 (C_2 and C_3) (*Z* isomer); 128.84 and 133.34 (C_2 and C_3) (*E*-isomer). Anal. Found: C, 78.96; H, 13.13. $C_{13}H_{26}O$ calcd.: C, 78.72; H, 13.21%.

*5-Methyl-hexa-2,4-dien-1-ol (**5d**) benzoate*

1. Reaction involving α-sulfonyl monoanions. To a stirred solution of sulfone **1d** (1.85 g, 8.8 mmol) in THF (25 ml) at −20 °C was added n-BuLi in hexane (1.6 *M*, 5.0 ml, 8.00 mmol). Stirring was continued for 15 min and epoxide **2** (0.716 g, 6.16 mmol) in THF (5 ml) added during 40 min. After an additional 2 h, the mixture was allowed to warm to room temperature and was set aside overnight. Water was added and the product was extracted with pentane. The extract was concentrated under a column, and the residue (ca. 2 ml) was cooled and diluted with methanol (10 ml) containing a trace of perchloric acid. After 1 h the mixture was diluted with water

and extracted with CH_2Cl_2. The extract was washed with water and concentrated under a column, to ca. 2 ml and pyridine (2 ml) and benzoyl chloride (1.73 g, 12.3 mmol) were successively added. The mixture was stirred at room temperature for 1 h and diluted with water. The product was isolated as described for the previous experiment and purified on SiO_2 (40 g, benzene–hexane, 1 : 1). The benzoate of **5d** was obtained (0.820 g, 57% yield) as a mixture of (*E*) and (*Z*) isomers in a 1 : 5 ratio; δ_H 7.91–7.23 (5H, m, aromat. H), 6.28 (1H, dd, $J_{3,2} = 11.3$, $J_{3,4} = 11.3$ Hz, C_3-H), 6.05 (1H, br d, $J_{4,3} = 11.4$ Hz, C_4-H), 5.41 (1H, dt, $J_{2,1} = 7.1$, $J_{2,3} = 11$ Hz, C_2-H), 4.85 (2H, br d, $J_{1,2} = 7.2$ Hz, C_1-H), 1.68 (3H, br s, CH_3), 1.62 (3H, br s, CH_3) (*Z*-isomer); 7.91–7.23 (5H, m, aromat. H), 6.44 (1H, dd, $J_{3,2} = 15.1$, $J_{3,4} = 11$ Hz, C_3-H), 5.71 (1H, br d, $J_{4,3} = 11$ Hz, C_4-H) 5.59 (1H, dt, $J_{2,1} = 6.7$, $J_{2,3} = 15.1$ Hz, C_2-H), 4.70 (2H, br d, $J_{1,2} = 6.7$ Hz, C_1-H), 1.68 (3H, br s, CH_3), 1.62 (3H, br s, CH_3) (*E*-isomer); δ_C 18.11, 26.37 (C_7 and C_6), 61.02 (C_1), 119.56, 121.25, 129.02, 138.79 (C_2–C_5), 128.26, 129.59, 130.51, 132.73, 132.8 (aromat. C), 166.27 (CO) (*Z*-isomer); 18.33, 25.98 (C_7 and C_6), 65.79 (C_1), 123.46, 124.01, 131.53, 137.51(C_2-C_5), 128.26, 129.59, 130.51, 132.73, 132.8(aromat. C), 166.09(CO) (*E*-isomer).

2. Reactions involving dianions. To a stirred solution of sulfone **1d** (0.95 g, 4.52 mmol) in THF (20 ml) at 0 °C, a solution of n-BuLi in hexane (1.6 *M*, 5.7 ml, 9.04 mmol) was added during 10 min. After an additional 30 min the mixture was cooled to −20 °C and a solution of epoxide **2** (0.394 g, 3.39 mmol) in THF (3 ml) was added during 10 min. The mixture was stirred at −20 °C for 2 h and then at room temperature for 18 h. The clear solution was cooled to −78 °C and treated with a solution of *p*-nitrobenzoic acid (0.944 g, 5.65 mmol) in THF (8 ml). The cooling was moderated, and after 1 h at −50 °C a precipitate started to separate. The mixture was allowed to warm to room temperature and stirring continued for a further 5 h. Water (40 ml) was added and the product was extracted with pentane (3 × 30 ml). The extract was concentrated under a fractionating column to ca. 3 ml. The residue was diluted with methanol (20 ml) containing a catalytic amount of *p*-TSA monohydrate and set aside. After 45 min the mixture was diluted with water (30 ml) and extracted with CH_2Cl_2 (3 × 30 ml). The extract was washed with a sodium carbonate solution and dried and the distilled off under a column., The residue (ca. 3 ml) was diluted with CH_2Cl_2 (20 ml) containing pyridine (4 ml) and treated with benzoyl chloride (0.953 g, 6.78 mmol) in CH_2Cl_2 (5 ml). The mixture was stirred at room temperature for 1 h, water (40 ml) then added, and the product extracted with pentane (3 × 30 ml). The pentane solution was washed successively with 5% aq. H_2SO_4 (50 ml), saturated aqueous $NaHCO_3$ (50 ml) and water (3 × 50 ml) and the solvent then evaporated in vacuo. The residue was chromatographed on SiO_2 (40 g, benzene–pentane, 1 : 3) to give the benzoate of 5d (0.380 g, 48% yield) as a mixture of (*E*) and (*Z*) isomers in a 1.2 : 1 ratio.

Cinnamyl alcohols

1. Reaction involving benzyl phenyl sulfone and an excess of oxirane 2. To a stirred solution of sulfone **1e** (0.697 g, 3 mmol) in THF (25 ml), at −20 °C was added n-BuLi in hexane (1.5 *M*, 2 ml, 3 mmol). Stirring was continued for 15 min and the epoxide **2** (0.698 g, 6 mmol) was slowly added. After additional 3 h the mixture was allowed to warm to room temperature and set aside overnight. Hydrochloric acid (1%, 20 ml) was added, mixture stirred for 15 min, and the product extracted with CH_2Cl_2. The solvent was removed and the residue chro-

matographed on SiO_2 (50 g, CH_2Cl_2 and then CH_2Co_2–MeOH, 50:1) to give alcohols **5e** (0.308 g, 76% yield, calcd. against the sulfone) as a mixture of (*E*) and (*Z*) isomers in a 1:1.2 ratio; δ_H 7.46–7.15 (5H, m, aromatic H), 6.49 (1H, dt, $J_{3,2} = 11.8$, $J_{3,1} = 1.7$ Hz, C_3-H), 5.82 (1H, dt, $J_{2,3} = 11.8$, $J_{2,1} = 6.3$ Hz, C_2-H), 4.38 (2H, dd, $J_{1,2} = 6.3$, $J_{1,3} = 1.7$ Hz, C_1-H) (*Z*-isomer); 7.46–7.15 (5H, m, aromatic H), 6.55 (1H, dt, $J_{3,2} = 15.9$, $J_{3,1} = 1.5$ Hz, C_3-H), 6.30 (1H, dt, $J_{2,3} = 15.9$, $J_{2,1} = 5.7$ Hz, C_2-H), 4.24 (2H, dd, $J_{1,2} = 5.7$, $J_{1,3} = 1.5$ Hz, C_1-H) (*E*-isomer);

2. Reaction involving an excess of sulfone. To a stirred of sulfone **1e** (0.917 g, 3.94 mmol) in THF (20 ml), at −20 °C, a solution of n-BuLi in hexane (1.6 *M*, 2.1 ml, 3.35 mmol) was added during 10 min. Stirring was continued for 15 min and then epoxide **2** (0.349 g, 3 mmol) was added during 10 min. After an addition 3 h, the mixture was allowed to warm to room temperature and was set aside for 14 h. A yellow precipitate separated. The mixture was diluted with water (30 ml) and extracted with CH_2Cl_2 (3 × 30 ml). The solvent was evaporated to leave semicrystalline residue. TLC analysis of this material indicated the present of starting sulfone (**1e**), cinnamyl alcohols, and another compound. The mixture was chromatographed on SiO_2 (30 g, CH_2Cl_2) to give:

(a) *trans*-Stilbene (0.149 g, 40% yield); colorless crystals, m.p. 125–127 °C, showing no depression upon admixing of an authentic sample; δ_H 7.51–7.23 (10H, m, aromatic H), 7.1 (2H, s, vinylic H);

(b) Starting sulfone **1e** (0.259 g).

Attempts to isolate minor components of the mixture were unsuccessful.

Reaction of isopropyl phenyl sulfone (9) with oxirane 2

To a stirred solution of sulfone **9** (1.995 g, 13.46 mmol) in ether (20 ml), at −20 °C was added n-BuLi in hexane (1.6 *M*, 8.4 ml, 13.5 mmol). Stirring was continued for 15 min and epoxide **2** (1.258 g, 10.82 mmol) in ether (5 ml) then added during 1 h. After an additional 1 h, the mixture was allowed to warm to room temperature and set aside overnight. Methanol (10 ml) containing 70% perchloric acid (1.1 ml) was then added, the mixture was stirred for 1 h and the product was taken up in CH_2Cl_2 (3 × 50 ml). The solvent was distilled off under a column and the residue diluted with CH_2Cl_2 (15 ml) and treated successively with pyridine (1.6 ml, 20 mmol) and benzoyl chloride (1.565 g, 11 mmol) in CH_2 cl_2 (5 ml). The mixture was stirred for 1 h then diluted with water (30 ml) and extracted with pentane (3 × 50 ml). The extract was washed successively with 10% H_2SO_4, aqueous $NaHCO_3$, and water, and the solvent evaporated off in vacuo. The residue was chromatographed on SiO_2 (40 g, benzene–hexane, 1:1, then benzene–ethyl acetate, 9:1) to give:

(a) Prenyl benzoate (0.641 g, 31% yield); δ_H 8.06–7.26 (5H, m, aromat. H), 5.48 (1H, br t, $J = 7.2$ Hz, C_2-H), 4.83 (2H, br d, $J = 7.2$ Hz, C_1-H), 1.79 (3H, br s, CH_3), 1.77 (3H, br s, CH_3); δ_C 18.00, 25.67 (C_4 and C_5), 61.77 (C_1), 118.72, 138.96 (C_2 and C_3), 128.20, 129.46, 129.59, 130.53, 132.67 (aromatic C), 166.56 (CO).

(b) Benzoate of 3-benzenesulfonyl-3-methyl-1-trimethylsilyl-butan-1-ol (**11** (0.477 g, 11% yield); m.p. 103–105 °C (methanol); δ_H 8.0–7.45 (10H, m, aromat. H), 5.24 (1H, dd, $J_{1,2a} = 11.5$, $J_{1,2b} = 1.5$ Hz, C_1-H), 2.39 (1H, dd, $J_{2a,2b} = 14.6$, $J_{21,1} = 11.5$ Hz, C_2-Ha), 2.13 (1H, br d, $J_{2b,2a} = 14.6$ Hz, C_2-Hb), 1.34 (3H, s, CH_3), 1.22 (3H, s, CH_3), 0.07 (9H, s, $SiCH_3$); δ_C −3.89 (SiC), 20.16, 21.0 (C_4 and C_5), 34.47 (C_2), 63.42 and 65.24 (C_1 and C_3), 128.14 and 135.14 (aromat. C), 166.16 (CO). Anal.

Found: C, 62.39; H, 7.11. $C_{21}H_{28}O_4SSi$ calcd.: C, 62.33; H, 6.97%.
(c) Carbinol **11** (0.988 g, 34% yield); δ_H 7.91–7.40 (5H, m, aromat. H), 3.63 (1H, dd, $J_{1,2a} = 11.3$, $J_{1,2b} = 1.5$ Hz, C_1-H), 2.05 (1H, dd, $J_{2a,1} = 11.3$, $J_{2a,2b} = 15.3$ Hz, C_2-Ha), 1.81 (1H, dd, $J_{2b,2a} = 15.3$, $J_{2b,1} = 1.5$ Hz, C_2-Hb), 1.41 (3H, s, CH_3), 1.31 (3H, s, CH_3), 0.04 (9H, s, $SiCH_3$); δ_C −4.29 ($SiCH_3$), 21.73, 22.79 (C_4 and C_5), 38.82 (C_2), 61.09, 63.63 (C_1 and C_3), 128.64, 130.55, 133.59, 135.31 (aromat. C).

The Brook rearrangement of sila-carbinol (11)

1. A mixture of carbinol **11** (0.300 g, 1.0 mmol), anhydrous ether (7 ml), and sodium hydride (0.200 g, 8.3 mmol; prepared from a suspension of sodium hydride in mineral oil by repeated washing with pentane and drying in a stream of argon) was stirred at room temperature for 24 then filtered through Celite. The filtrate was evaporated to dryness and the residue chromatographed on SiO_2 (15 g, hexane–ethyl acetate, 9 : 1 gradually to 1 : 1). Compound **12** was obtained (0.137 g, 60% yield) as an oil. Distillation of the product 160 °C/0.01 Torr, using a cold-finger apparatus, gave an analytical sample; δ_H 7.90 (2H, m, $C_{2'}$ and $C_{6'}$-H), 7.67 (1H, tt, $J_1 = 7.5$, $J_2 = 1.2$ Hz, $C_{4'}$-H) and 7.57 (2H, m, $C_{3'}$- and $C_{5'}$-H), 3.85 (2H, m, C_1-H), 2.01 (2H, t, $J = 6.6$ Hz, C_2-H), 1.37 (6H, s, 2 CH_3). Anal. Found: C, 57.88; H, 7.25. $C_{11}H_{16}O_3S$ calcd.: C, 57.87; H, 7.05%.

2. In an analogous experiment carbinol **11** (0.300 g, 1 mmol), anhyd. ether (4 ml), HMPA (0.18 ml, 1.0 mmol) and sodium hydride (0.075 g, 3.1 mmol) were used. Work-up gave compound **12** (0.050 g, 30% yield). An attempt to isolate the volatile products of the reaction were unsuccessful.

3. A mixture of carbinol **11** (0.300 g, 0.1 mmol), anhydrous ether (7 ml), and sodium hydride (0.02 g, 0.83 mmol) was stirred at room temperature for 24 h then filtered through Celite. The filtrate was evaporated and the residue chromatographed on 3 TLC plates (20 × 20) with an 8 : 2 : 0.1 a mixture of hexane, ethyl acetate and triethyl amine as eluent. The spot containing the main product was extracted with ether containing 0.1% of triethylamine and the extract evaporated to dryness. TLC analysis of the residue showed the presence of two products, with $R_f = 0.3$ and $R_f = 0.02$. The ^1H NMR spectrum of this mixture displayed the signals of alcohol **12** (as described above) along with signals attributed to the O-trimethylsilyl derivative of alcohol **12**, δ_H 3.75 (2H, t, $J = 6.9$ Hz, C_1-H), 1.94 (2H, t, $J = 6.9$ Hz, C_2-H), 1.36 (6H, s, $2CH_3$), 0.09 (9H, s, $SiCH_3$); integration of signals pointed to a product ratio of 3 : 2.

Reaction of c-hexyl phenyl sulfone (13) with epoxide 2

To a stirred solution of sulfone **13** (2.90 g, 12.95 mmol) in THF (50 ml) at −20 °C a solution of n-BuLi in hexane (1.1 *M*, 11.7 ml, 12.9 mmol) was added dropwise. Stirring was continued for 15 min and epoxide **2** (1.0 g, 8.62 mmol) in THF (10 ml) added during 2.5 h. After a further 2 h the mixture was allowed to warm to room temperature and was set aside overnight. Water (10 ml) was added and the product extracted with CH_2Cl_2 (3 × 50 ml). The solvent was evaporated in vacuo and the residue (3.8 g) chromatographed on SiO_2 (120 g, toluene and the 19/1 toluene–ethyl acetate, as eluents) to give unchanged sulfone **13** (1.4 g) and 1-trimethylsilyl-2-(1′-benzenesulphonyl-cyclohexyl)-ethanol **14** (2.14 g, 73% yield); m.p. 104–105 °C (hexane); ν_{max}(KBr) 3350 (OH), 1300 (SO_2Ph), 1250 and 840

($SiMe_3$) cm^{-1}; δ_H 7.93 (2H, m, aromat. H), 7.68 (1H, m, aromat. H), 7.57 (2H, m, aromat. H), 4.05 (1H, d, $J = 2.5$ hz, OH), 3.69 (1H, m, X of ABX, C_1-H), 2.26 (1H, br d, $J = 13.2$ Hz), 2.02 and 1.99 (2H, AB of ABX, 2dd, $J_{2a,2b}$, $J_{2a,2b} = 16.8$, $J_{2a,1} = 11.3$, $J_{2b,1} = 1.2$ Hz, C_2-Ha and Hb), 1.8–1.5 (6H, m), 1.41–1.30 (1H, m), 1.22–1.02 (2H, m), 0.07 (9H, s, $SiCH_3$). Anal. Found: C, 60.04; H, 8.12. $C_{17}H_{28}O_3SSi$ calcd.: C, 59.96; H, 8.29%.

2-(1′-Benzenesulfonylcyclohexyl)-ethanol (15)

A mixture of silyl carbinol **14** (0.341 g, 1 mmol), tetrabutylammonium fluoride trihydrate (0.631 g, 2 mmol) and THF (5 ml) was stirred at 40 °C for 6 h and then diluted with water (2 ml). Work-up (extraction with CH_2Cl_2) gave carbinol **15** (0.215 g, 80% yield); ν_{max}(film) 3400 (OH) and 1285 (SO_2Ph) cm^{-1}; δ_H 7.89 (2H, m, aromat. H), 7.68 (1H, m, aromat. H) and 7.57 (2H, m, aromat. H), 3.93 (2H, t, $J = 6.8$ hz, C_1-H), 2.94 (1H, br s, OH), 2.07 (2H, t, $J = 6.8$ Hz, C_2-H), 183 (2H, br d, $J = 13.5$ Hz), 1.75–1.60 (5H, m), 1.43–1.27 (2H, m); δ_C 21.2, 24.6, 28.7, 31.9, 57.8 (C-1′), 65.8 (C-1), 128.7, 130.6, 133.6 and 134.8 (aromat. C).

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