

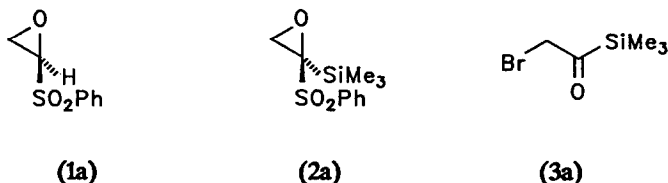
PREPARATION AND RING-OPENING REACTIONS OF 2-PHENYLSULPHONYL-2-TRIMETHYLSILYL OXIRANES

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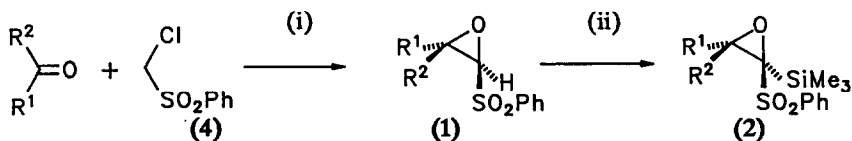
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Summary: Reaction of 2-phenylsulphonyl oxiranes (1) with butyllithium in the presence of chlorotrimethylsilane gave 2-phenylsulphonyl-2-trimethylsilyl oxiranes (2), which on treatment with $MgBr_2 \cdot Et_2O$ gave 2-bromoacylsilanes (3) and either bromovinyl sulphones (5) or α, β -unsaturated acylsilanes (6) and 2-trimethylsilyl carboxylic acids (7), depending on structure.

As part of our efforts to extend the synthetic utility of 2-phenylsulphonyl oxiranes (1),^{1,2,3} we have established that treatment of phenylsulphonyl oxirane (1a) with chlorotrimethylsilane and butyllithium in THF at $-102^\circ C$ gives 2-phenylsulphonyl-2-trimethylsilyl oxirane (2a).¹ Reaction of (2a) with magnesium bromide etherate then gave bromoacetyltrimethylsilane (3a) in good yield. In view of the recent interest in the synthesis,^{4,5,6} and synthetic utility,^{6,7} of 2-haloacylsilanes, we now report the results of our efforts to induce ring-opening of substituted 2-phenylsulphonyl-2-trimethylsilyl oxiranes (2) with $MgBr_2 \cdot Et_2O$.



The 2-phenylsulphonyl oxiranes (1) were easily prepared by Darzens reaction of chloromethyl phenylsulphone (4) with either aldehydes or ketones.⁸ *Trans* oxiranes are obtained from aldehydes, and mixtures of stereoisomers are obtained from unsymmetrical ketones. Treatment of each of these oxiranes with chlorotrimethylsilane and butyllithium⁹ then gave the corresponding 2-phenylsulphonyl-2-trimethylsilyl oxiranes (2) in high yield (Scheme 1, Table 1).¹⁰



Scheme 1. i, 50% aq. NaOH, $Et_3BnN^+Br^-$; ii, Me_3SiCl (2.5 equiv.), BuLi (1.8 equiv), THF, $-102^\circ C$.

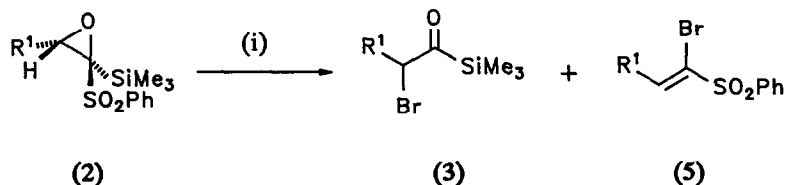
Table 1

R ¹	R ²	Phenylsulphonyl Oxirane	Yield %	Silyl Oxirane,	Yield %
Me	H	(1b)	73	(2b)	62 ^b
Et	H	(1c)	69	(2c)	61 ^b
Pr	H	(1d)	93	(2d)	72 ^b
Pr ^f	H	(1e)	99	(2e)	91
Bu	H	(1f)	90	(2f)	80 ^b
Ph	H	(1g)	69	(2g)	73
Me	Me	(1h)	96	(2h)	99
	Et/Me	(1i)	96 ^a	(2i)	92 ^a
Et	Et	(1j)	84	(2j)	93
	PhCH ₂ /Et	(1k)	35 ^a	(2k)	93 ^a
	(CH ₂) ₄	(1l)	85	(2l)	91
	(CH ₂) ₅	(1m)	100	(2m)	91

^a Chromatographically inseparable mixtures of diastereoisomers.

^b Small amounts of material silylated additionally at the *ortho*-position of the phenylsulphonyl group were also isolated.

We have found that those oxiranes derived originally from aldehydes (2b–2g) are less reactive than those derived from ketones (2h–2m) towards reaction with MgBr₂.Et₂O. Reaction of oxiranes (2b–2g) with magnesium bromide occurs only on prolonged exposure, to give a mixture of the 2-bromoacylsilanes (3b–3g) and the bromovinyl sulphones¹¹ (5b–5f) (Scheme 2, Table 2).¹² For those substrates (2b–2d) which react at room temperature, good yields of 2-bromoacyl silanes are obtained. When refluxing in THF is required to achieve consumption of starting material, the formation of bromovinyl sulphones (5) becomes a competing process. The latter compounds are derived by attack of bromide ion α to the phenylsulphonyl and trimethylsilyl groups, followed by elimination of trimethylsilanolate.¹³ Indeed, treatment of (2d) with MgBr₂.Et₂O in THF at reflux, rather than room temperature in Et₂O, led to a mixture of the α -bromoacylsilane (3d) and the bromovinyl sulphone (5d). Previous work has shown that nucleophilic attack on trimethylsilyl oxiranes by magnesium bromide occurs α to the silyl group,¹⁴ whereas attack on phenylsulphonyl oxiranes occurs at the β -position.^{1,2,3,15} In cases where attack at the β -position is hindered (e.g. in (2e)), the preference for β -attack in phenylsulphonyl oxiranes can be almost completely overcome.



Scheme 2. i, MgBr₂.Et₂O.

Table 2

R ¹	Silyl Oxirane	Time	Conditions	α -Bromoacylsilane	Yield %	Vinyl sulphone	Yield %
Me	(2b)	44h	r. t. Et ₂ O	(3b)	79	(5b)	0
Et	(2c)	20h	r. t. Et ₂ O	(3c)	75	(5c)	0
Pr	(2d)	48h	r. t. Et ₂ O	(3d)	77	(5d)	0
Pr ⁱ	(2e)	9d	THF reflux	(3e)	7	(5e)	64
Bu	(2f)	72h	THF reflux ^a	(3f)	41	(5f)	50
Ph	(2g)	46h	THF reflux	(3g)	2	(5g)	50

^a No detectable reaction at r.t. in THF.

Reaction of oxiranes (2h–2m), derived from ketones, with MgBr₂.Et₂O in ether occurred much more quickly, taking place at temperatures ranging from -18 °C to room temperature, and leading to the formation of the corresponding α -bromoacylsilanes (3h–3m) as the major products, together with variable amounts of the α,β -unsaturated acylsilanes (6h–6m).^{1,2} The mass balance was composed of the α -trimethylsilyl carboxylic acids (7h–7m), presumably formed by rearrangement¹⁶ (Scheme 3, Table 3). Exposure of the α -bromoacylsilane (3m) to the reaction conditions did not lead to the α,β -unsaturated acylsilane (6m). This result, and the formation of rearrangement products, supports the intermediacy of a carbocation, formed by magnesium ion induced cleavage of the O–1 to C–3 bond. Clearly, this process is favoured in oxiranes (2h–2m), which can give rise to tertiary carbocations.

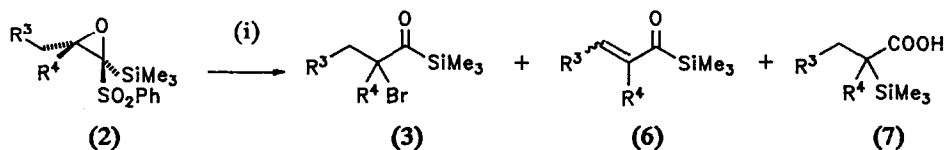
Scheme 3. i, MgBr₂.Et₂O, Et₂O

Table 3

Silyl Oxirane	R ³	R ⁴	Time, h	Temp., °C	2-Bromoacyl Silane	Yield %	Unsaturated Acylsilane	Yield %
(2h)	H	Me	4	20	(3h)	49	(6h)	0
(2i) ^a	Me	Me	3	0	(3i)	46	(6i)	6
(2j)	Me	Et	5½	0	(3j)	40	(6j)	15
(2k) ^a	Me	PhCH ₂	66	4	(3k)	64	(6k)	8 ^b
(2l)	(CH ₂) ₃		4	0	(3l)	57	(6l)	8
(2m)	(CH ₂) ₄		120	-18	(3m)	56	(6m)	15

^a These compounds are mixtures of diastereoisomers, of which only one is drawn.

^b The corresponding regioisomer (R³ = Ph, R⁴ = Et) was isolated in 3% yield; the reason for the preferential formation of the less conjugated isomer is unclear.

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10. The 2-phenylsulphonyl oxirane (1) (4.42 mmol) was dissolved in dry THF (50 ml) under nitrogen. Chlorotrimethylsilane (11.05 mmol) was added and the solution was cooled to $-102\text{ }^{\circ}\text{C}$ (internal temperature). Butyllithium (7.96 mmol, solution in hexanes) was added dropwise, keeping the internal temperature below $-100\text{ }^{\circ}\text{C}$, and then aq. NH_4Cl (10%, 10 ml) was added immediately. The organic layer was separated, and the aqueous layer extracted with CH_2Cl_2 (3 x 30 ml). The combined organic layers were dried (MgSO_4), solvent was removed, and the residue purified by flash chromatography (eluent 10:1 40–60 petrol: ethyl acetate).
11. For previous syntheses of bromovinyl sulphones, see: J.C. Phillips, M. Aregullin, M. Oku, and A. Sierra, *Tetrahedron Letts.*, 1974, 4157; and P. Carlier, Y. Gelas-Mialhe, and R. Vessière, *Can. J. Chem.*, 1977, 55, 3190.
12. The silyl oxirane (1 mmol) was dissolved in dry THF or Et_2O (10 ml) and treated with $\text{MgBr}_2 \cdot \text{Et}_2\text{O}$ (1.2 mmol). The mixture was treated at the temperature and for the period indicated in tables 2 and 3. Following addition of pH7 phosphate buffer, the mixture was extracted with diethyl ether (3 x 20 ml). The combined organic extracts were dried (MgSO_4), solvent was removed (care: the α -bromoacylsilanes are relatively volatile), and the residue was purified by flash chromatography (eluent 80:1 30–40 petrol: diethyl ether). The structures of the products were established by spectroscopic methods. In particular, all acylsilanes showed characteristic absorptions in their i.r. spectra due to the carbonyl stretch. The α -bromoacylsilanes (3b–f) exhibited a stretch in the range 1646 to 1648 cm^{-1} . The more substituted α -bromoacylsilanes (3h–m) showed stretches in the range 1636 to 1643 cm^{-1} . Finally, the range for the α,β -unsaturated acylsilanes (6i–m) was 1585 to 1605 cm^{-1} .
13. The bromovinyl sulphones were isolated as single stereoisomers assigned as *Z* on the basis of the chemical shift of the vinylic proton. This stereoisomer would be formed by *syn* elimination of trimethylsilylanolate from the initially formed β -hydroxy silane. For a recent discussion of the mechanism of the Peterson olefination reaction, see: P.F. Hudrlik, E.L.O. Agwaramgbo, and A.M. Hudrlik, *J. Org. Chem.*, 1989, 54, 5613.
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