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

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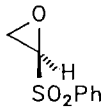
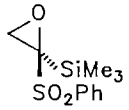
Summary: Reaction of 2-phenylsulphonyl oxiranes (1) with butyllithium in the presence of chlorotrimethylsilane gave 2-phenylsulphonyl-2-trimethylsilyl oxiranes (2), which on treatment with $MgBr_2.Et_2O$ gave 2-bromoacylsilanes (3) and either bromovinyl sulphones (5) or α,β-unsaturated acylsilanes (6)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

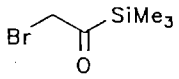
As part of our efforts to extend the synthetic utility of 2-phenylsulphonyl oxiranes (1),[1,2,3] we have established that treatment of phenylsulphonyl oxirane (1a) with chlorotrimethylsilane and butyllithium in THF at -102 °C gives 2-phenylsulphonyl-2-trimethylsilyl oxirane (2a).[1] Reaction of (2a) 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 $MgBr_2.Et_2O$.



(1a)

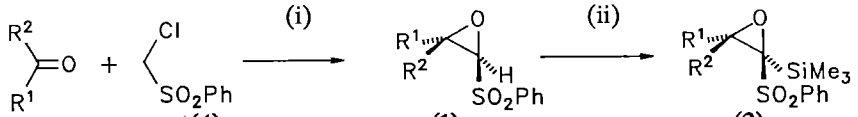


(2a)



(3a)

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 butyllithium[9] then gave the corresponding 2-phenylsulphonyl-2-trimethylsilyl oxiranes (2) in high yield (Scheme 1, Table 1).[10]



(4) (1) (2)

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

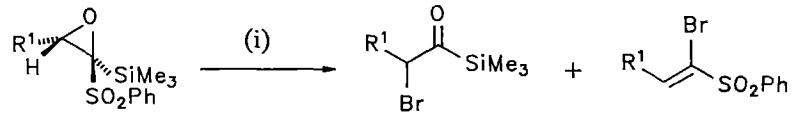
Table 1

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^i	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 $MgBr_2.Et_2O$. 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 sulphones[11] **(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 $MgBr_2.Et_2O$ in THF at reflux, rather than room temperature in Et_2O, 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.



(2) (3) (5)

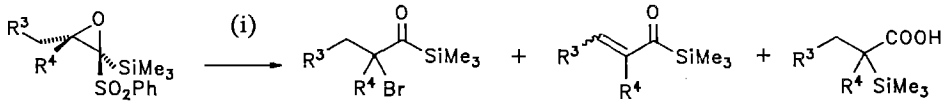
Scheme 2. i, $MgBr_2.Et_2O$.

Table 2

R^1	Silyl Oxirane	Time	Conditions	α-Bromoacylsilane	Yield %	Vinyl sulphone	Yield %
Me	(2b)	44h	r.t. Et_2O	(3b)	79	(5b)	0
Et	(2c)	20h	r.t. Et_2O	(3c)	75	(5c)	0
Pr	(2d)	48h	r.t. Et_2O	(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 $MgBr_2.Et_2O$ 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)**.[12] The mass balance was composed of the α–trimethylsilyl carboxylic acids **(7h–7m)**, presumably formed by rearrangement[16] (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.



(2) (3) (6) (7)

Scheme 3. i, $MgBr_2.Et_2O$, Et_2O

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 (R^3 = Ph, R^4 = Et) was isolated in 3% yield; the reason for the preferential formation of the less conjugated isomer is unclear.

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9. For the first example of this process, see: J.J. Eisch and J.E. Galle, *J. Organomet. Chem.*, 1976, **121**, C10; J.J. Eisch and J.E. Galle, *J. Organomet. Chem.*, 1988, **341**, 293.
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 °C (internal temperature). Butyllithium (7.96 mmol, solution in hexanes) was added dropwise, keeping the internal temperature below −100 °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. Philips, 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 $MgBr_2.Et_2O$ (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 trimethylsilanolate 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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