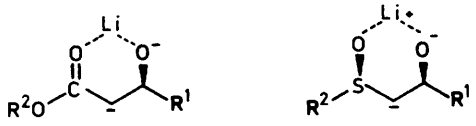
Unusual Stereoselection in the Reaction of Dianions Derived from 1-Phenylsulphonylalkan-2-ols with Electrophilic Reagents

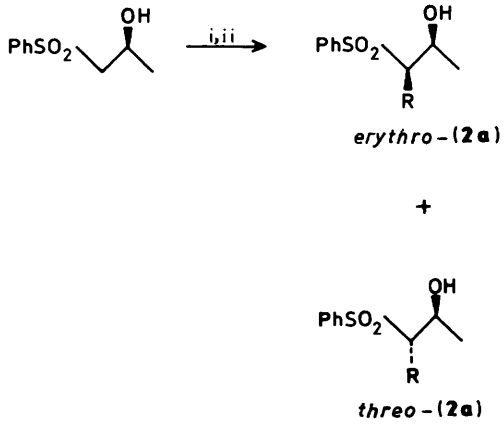
Rikuhei Tanikaga,* Ken Hosoya, and Aritsune Kaji
Department of Chemistry, Faculty of Science, Kyoto University, Kitashirakawa, Sakyo-ku, Kyoto 606, Japan

The stereochemistry in the reaction of dianions of 1-phenylsulphonylalkan-2-ols (**1**) with electrophilic reagents such as alkyl halides and aldehydes is discussed. The reaction takes place regioselectively at the α-position to the sulphonyl group to form a new chiral centre. In tetrahydrofuran the sterically more crowded *erythro*-isomer is obtained as the major product in a good diastereoisomeric ratio (50—100% d.e.). Additives such as HMPA and bulky diamines greatly influence the stereoselectivity of the reaction. The co-ordination of tetrahydrofuran molecules with a metal cation is considered to play an important role in the reaction.

Dianions are widely used in organic synthesis, but the stereochemistry of their carbon–carbon bond formation has not fully been elucidated. It has been briefly reported that the dianions of β-hydroxyesters or β-hydroxy sulphoxides react with electrophilic reagents to afford the *threo*-isomers as major products;[1,2] these findings may be explained by the intramolecular chelation[3] between an alkoxide anion and a polar carbonyl or sulphinyl group *via* a lithium counter cation (see below).



The dianions[4–8] of 1-phenylsulphonylalkan-2-ols (β-hydroxy sulphones) have also been widely used in organic synthesis,[9,10] and Kozikowski's group recently reported that treatment of the dianions of 1-phenylsulphonylpropan-2-ol (**1a**) with alkyl halides (*e.g.* methyl iodide or allyl bromide) in tetrahydrofuran (THF) generated preferentially the sterically more crowded *erythro*-isomers (Scheme 1).[11]



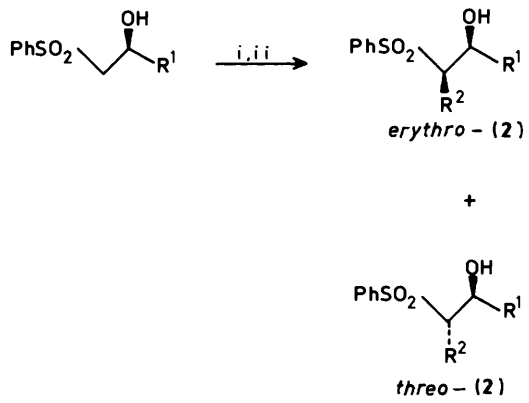
Scheme 1. *Reagents:* i, BuLi (2 equiv.); ii, alkyl halide

These results are quite different from those obtained in the reaction of dianions derived from β-hydroxy esters or β-hydroxy sulphoxides and suggest that the reaction of the dianion of (**1a**) may proceed through a different stereochemical course.

Here we report the stereochemistry in the reaction of the dianions of 1-phenylsulphonyl alkan-2-ols with electrophilic reagents such as alkyl halides, dimethyl sulphate, and aldehydes under a variety of conditions, and discuss the conformation of the dianion in the reaction.

Results and Discussion

When a solution of the dianion generated from 1-phenylsulphonylundecan-2-ol (**1c**) and butyl-lithium (2.2 equiv.) in THF at −78 °C[12] was quenched with D_2O, a product monodeuteriated (**1c**) at the position α to the sulphonyl group was obtained quantitatively, but the stereoselectivity in this lithiation step could not be determined because its diastereoisomers were not separable by any methods. The alkylation of the dianion of (**1**) was carried out as in Scheme 2.



Scheme 2. *Reagents:* i, BuLi (2 equiv.); ii, R^2X or $(MeO)_2SO_2$

After transforming compounds (**1**) into their corresponding dianions in THF at −78 °C, treatment of the dianions with alkyl halides or dimethyl sulphate afforded, as expected, the products (**2**) alkylated at the position α to the sulphonyl group in good yields. The configurations of these products were assigned on the basis of the coupling constant $J_{H_\alpha H_\beta}$ † by 400 MHz ^{1}H n.m.r. analysis. The results are listed in Table 1.

† Since the hydroxy and the phenylsulphonyl groups of (**1**) are close to each other *via* intramolecular hydrogen bonding, the coupling constant $J_{H_\alpha H_\beta}$ in *erythro*-(**2**) must be smaller than that in *threo*-(**2**). See, E. Brunet, J. L. Garcia Ruano, M. C. Martinez, and J. D. Rodriguez, *Tetrahedron*, 1984, **40**, 2023. W. E. Truce and T. C. Klingler, *J. Org. Chem.*, 1970, **35**, 1834. M. Julia, *et al.*, *Tetrahedron*, 1986, **42**, 2475.

Table 1. Alkylation reaction of the dianion of (**1**)

Run	R^1 (**1**)	R^2X	(**2**)	Yield (%)[a]	*erythro*:*threo*
1	Me (**1a**)[b]	MeI	(**2a**)	98	51:49[c]
2	Me (**1a**)[b]	$(MeO)_2SO_2$	(**2a**)	96	83:17[c]
3	Me (**1a**)[b]	EtI	(**2b**)	57	61:39[c]
4	Me (**1a**)[b]	$C_8H_{17}I$	(**2c**)	45	83:17[c]
5	Me (**1a**)[b]	CH_2=$CHCH_2Br$	(**2d**)	83	73:27[d]
6	Me (**1a**)[b]	Me_2C=$CHCH_2Br$	(**2e**)	72	78:22[c]
7	Bu^i (**1b**)	MeI	(**2f**)	72	78:22[d]
8	Bu^i (**1b**)	CH_2=$CHCH_2Br$	(**2g**)	78	80:20[d]
9	C_9H_{19} (**1c**)	MeI	(**2h**)	72	78:22[d]
10	C_9H_{19} (**1c**)	$(MeO)_2SO_2$	(**2h**)	87	92:8[d]
11	C_9H_{19} (**1c**)	CH_2=$CHCH_2Br$	(**2i**)	81	85:15[d]
12	CH_2Ph (**1d**)	MeI	(**2j**)	62	85:15[d]
13	CH_2Ph (**1d**)	CH_2=$CHCH_2Br$	(**2k**)	69	>98:2[d]

[a] Isolated yield. [b] Enantiomerically pure (2*S*)-(**1a**) was used. [c] The ratio was determined by h.p.l.c. analysis. [d] The ratio was determined by the yield of each diastereoisomer isolated.

Table 2. Effects of additives on the alkylation reaction run

Run	(**1**)[a]	R^2X	Solvent	Additive (equiv.)	Yield (%)	*erythro*:*threo*
1	(**1a**)	CH_2=$CHCH_2Br$	THF	None	83[b]	73:27[c]
2	(**1a**)	CH_2=$CHCH_2Br$	THF	HMPT (2)	79[b]	58:42[d]
3	(**1a**)	CH_2=$CHCH_2Br$	Ether	None	7[e]	52:48[d]
4	(**1a**)	CH_2=$CHCH_2Br$	Ether	HMPT (2)	83[b]	51:49[d]
5	(**1a**)	CH_2=$CHCH_2Br$	THF	TMEDA (2)	82[b]	85:15[d]
6	(**1a**)	CH_2=$CHCH_2Br$	THF	DABCO (2)	67[b]	84:16[d]
7	(**1c**)	MeI	THF	None	40[e]	76:24[d]
					72[f]	78:22[f]
8	(**1c**)	MeI	Ether	None	28[f]	58:42[f]
9	(**1c**)	MeI	Ether	THF (1)	50[f]	82:18[f]
10	(**1c**)	MeI	THF	HMPT (2)	72[e]	56:44[d]
11	(**1c**)	MeI	THF	TMEDA (2)	35[e]	72:28[d]
12	(**1c**)	MeI	THF	12-crown-4 (2)	17[e]	60:40[d]

[a] R^1 as shown in Table 1. [b] Isolated yield. [c] Determined by the yield of each diastereoisomer isolated. [d] Determined by h.p.l.c. [e] The reactions were carried out at −78 °C and quenched in 30 min. [f] After 30 min at −78 °C, the reaction mixture was warmed to room temperature over 2 h and then quenched.

Interestingly in these alkylation reactions, the sterically more crowded *erythro*-isomers were always obtained as major isomers. Although the methylation of (**1a**) with methyl iodide (run 1) yielded a 51:49 *erythro*:*threo* diastereoisomeric mixture[11] the methylation of (**1c**) (run 9) and (**1d**) (run 12) yielded 78:22 and 85:15 diastereoisomeric mixtures, respectively, probably because of the steric effect of the alkyl side chain of (**1**). Similar effects were observed in the allylation reactions (run 5, 8, 11, and 13), and especially with (**1d**) where a bulky benzyl side chain produced only *erythro*-(**2k**). The *erythro*:*threo* ratio increased with increasing bulkiness of the alkylating reagent [*e.g.* methylation of (**1a**) with methyl iodide (run 1) < that with dimethyl sulphate (run 2), ethylation of (**1a**) (run 3) < octylation of (**1a**) (run 4), methylation of (**1c**) with methyl iodide (run 9) < that with dimethyl sulphate (run 10), and methylation of (**1d**) (run 12) < allylation of (**1d**) (run 13)]. These stereoselections are kinetically controlled because no isomerization was observed on treatment of the isolated *erythro*-isomer (**2d**) with butyllithium (2.2 equiv.) at room temperature. It may be concluded that the bulkiness of the alkyl side chain of (**1**) and the alkylating reagent influences the unusual stereoselection.

Effects of Additives on the Alkylation Reactions.—The effects of additives on the allylation reaction of (**1a**) and methylation reaction of (**1c**) were investigated. The results are listed in Table 2.

When bulky *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) or diazabicyclo[2.2.2]octane (DABCO) having the ability to coordinate with lithium cation[13] were added in THF, the *erythro*-isomers were obtained as major products in good diastereoisomeric ratios [as for reactions in the absence of additives (runs 5, and 6, and 11)]. On the other hand, when hexamethylphosphoric triamide (HMPT) forming the 'bare' solvent separated anion[14] or lithium-selective ionophore 12-crown-4[15] were employed as additives, stereoselection was found to be poor (runs 2, 9, and 12). Although the stereoselectivity was not observed when diethyl ether (ether) instead of THF (run 3 and 8) was used, addition of 1 equiv. of THF in ether led to high stereoselectivity. These results strongly suggested that lithium counter cations, THF solvent, and bulky diamine additives influence the stereoselection.

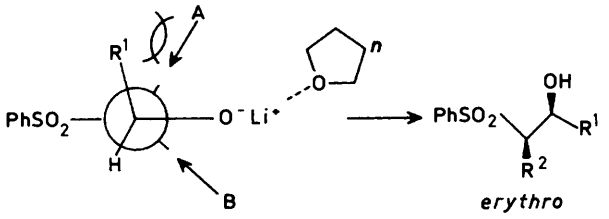
Recently, the co-ordination of THF molecules with lithium counter cations has been observed in the reaction of carbanions

Table 3. Reaction of the dianions of (1) with aldehydes

Run	(1)[a]	R^2	(3)	Yield (%)[b]	Diastereoisomer ratio
1	(1a)	C_9H_{19}	(3a)	82	80:20[c]
2	(1a)	$C_{11}H_{23}$	(3b)	73	80:20[d]
3	(1a)	$-CH_2CH(Me)(CH_2)_2CH{=}Me_2$	(3c)	78	*e*
4	(1b)	C_9H_{19}	(3d)	52	80:20[c]
5	(1b)	$C_{11}H_{23}$	(3e)	49	81:19[c]
6	(1b)	$-CH_2CH(Me)(CH_2)_2CH{=}Me_2$	(3f)	45	*e*
7	(1c)	Pr	(3g)	84	64:36[d]

[a] R^1 as shown in Table 1. [b] Isolated yield. [c] Determined by h.p.l.c. analysis. [d] Determined by the yield of each diastereoisomer. [e] Not determined.

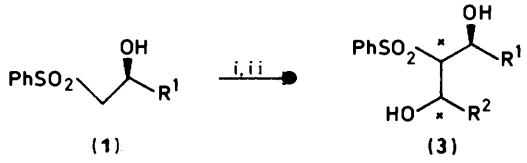
in THF.[16] If this co-ordination occurs during the reaction of the dianion, the bulky phenylsulphonyl group and the alkoxide anion co-ordinating some THF molecules *via* the lithium counter cation may be located in the *anti*-periplanar position because of the steric repulsion (Scheme 3). The alkylation



Scheme 3.

reaction must, therefore, proceed *via* reagent attack from the sterically less hindered site B rather than site A to give an *erythro*-isomer (2) as a major product (see Table 4 for analytical data). All findings in the alkylation reactions listed in Table 1 and 2 strongly support this conformation of the dianion of (1). It may be concluded that the chelating ability of a sulphonyl group is lower than that of the polar sulphinyl and carbonyl groups, and the co-ordinating ability of THF may play an important role. These stereoselections may be peculiar to the reaction of the dianion of (1).

Reaction with Aldehydes.—Reactions were carried out in THF at −78 °C and the 1,3-diols (3) were obtained in good yield (Scheme 4). The results are listed in Table 3, analytical data



Scheme 4. *Reagents:* i, BuLi (2 equiv.); ii, R^2CHO

are given in Table 4. Since these 1,3-diols have produced two additional chiral centres, four kinds of diastereoisomers may be obtained, but only two of them were detected by h.p.l.c. analysis,* and were separated by silica gel column chromatography. Their n.m.r. spectra revealed that the major isomer had a 1,3-*syn* conformation and the minor isomer had a 1,3-*anti* conformation,† and that the stereochemistry at the α-position to the sulphonyl group in both isomers was the same as that of (2). A diastereo-face differentiating reaction is observed at moderate rate.

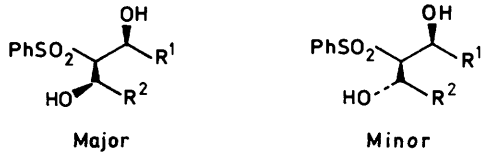
Table 4. Data for compounds (2) and (3)

Product[a]	Formula	Calculated (%) C	Calculated (%) H	Found (%) C	Found (%) H
(2a)	$C_{10}H_{14}O_3S$	56.05	6.59	56.15	6.5
(2b)	$C_{11}H_{16}O_3S$	57.87	7.06	57.9	7.35
(2c)	$C_{17}H_{28}O_3S$	65.35	9.03	65.1	9.25
(2d)	$C_{12}H_{16}O_3S$	59.97	6.71	60.25	7.1
(2e)	$C_{14}H_{20}O_3S$	62.66	7.51	62.3	7.75
(2f)	$C_{13}H_{20}O_3S$	60.91	7.86	61.15	7.7
(2g)	$C_{15}H_{22}O_3S$	63.80	7.85	64.0	8.0
(2h)	$C_{18}H_{30}O_3S$	66.22	9.26	66.0	9.1
(2j)	$C_{16}H_{32}O_4S$	66.18	6.25	66.0	6.25
(3a)	$C_{19}H_{32}O_4S$	64.01	9.05	64.0	9.3
(3b)	$C_{21}H_{36}O_4S$	65.59	9.44	65.9	9.2
(3c)	$C_{19}H_{30}O_4S$	64.37	8.53	64.35	8.55
(3d)	$C_{22}H_{38}O_4S$	66.29	9.61	65.95	9.4
(3e)	$C_{24}H_{42}O_4S$	67.56	9.92	67.2	10.0
(3f)	$C_{22}H_{36}O_4S$	66.63	9.15	66.35	8.85
(3g)	$C_{21}H_{36}O_4S$	65.59	9.44	65.15	9.0

[a] All products were diastereoisomeric mixtures.

These facts indicated that the reactions of the dianions of (1) with aldehydes proceed *via* a similar stereochemical course to the alkylation reactions, and also that the chelation of the carbonyl group of aldehydes with the lithium cation may play an important role in the stereoselection at the other chiral point.

Recently, it has been reported that in a lithiated α-sulphonyl carbanion the lithium counter cation is linked to an oxygen atom of a sulphonyl group by an enol type chelation.[15] Therefore, an aldehyde approaching the reaction centre is

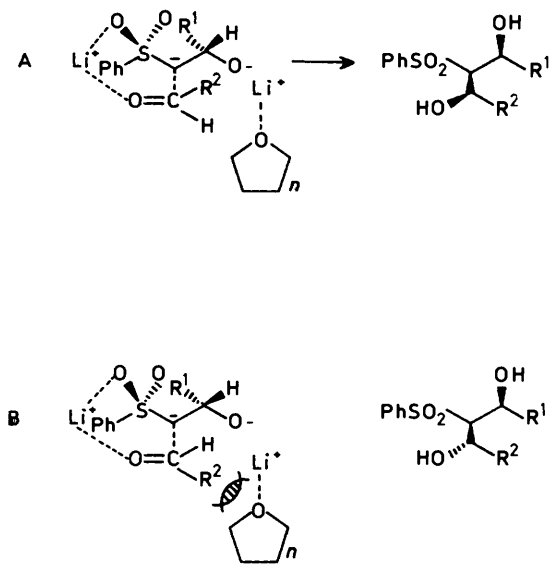


assumed to form a six-membered ring chelation system as shown in Scheme 5.

Reaction as given in B might be suppressed due to steric repulsion between the alkyl group of an aldehyde and THF co-ordinating an alkoxide group, and the reaction from the other side at a reaction centre also be greatly suppressed owing to

* We could separate all four diastereoisomers, which were obtained by another method, on an h.p.l.c. column and hence confirm that only two diastereoisomers were formed in the reaction of the dianion of (1).

† The isolated products, major and minor (3b), were converted readily into acetonides and their configurations established on the basis of coupling constants in 400 MHz ^1H n.m.r. spectra of acetonide. See, A. Hampton, *J. Am. Chem. Soc.*, 1961, **83**, 3640.



Scheme 5.

steric hindrance of an alkyl side chain R^1 of (**1**). Consequently, the reaction proceeds as shown in A to give the 1,3-*syn* isomer as a major product.

Experimental

^{1}H N.m.r. spectra were recorded on JEOL Model PS-100 (100 MHz) or JEOL Model JMN-FX 400 (400 MHz) instruments; chemical shifts (δ) are expressed in p.p.m. relative to tetramethylsilane. I.r. spectra were measured with a Hitachi Model 215 spectrometer. Mass spectra were recorded with a JEOL JMS-DX-300 spectrometer. H.p.l.c. analyses were carried out on a Shimadzu LC-6A system containing a 7125 valve loop injector (Rheodyne, Berkeley, CA, USA), and an ODS column or a PYE column[17] in aqueous methanol.

THF and ether were dried by standard techniques and distilled under argon. Commercial butyl-lithium in hexane was standardized by the method of Kofron.[18] Alkyl halides, aldehydes, and the additives were purified by standard techniques. Enantiomerically pure (2*S*)-1-phenylsulphonylpropan-2-ol (**1a**) and other 1-phenylsulphonylalkan-2-ols (**1b**—**d**) were prepared using reported methods.[19,12]

General Procedure for Alkylation of (**1a**—**d**).—Under an atmosphere of argon, BuLi (2.2 mmol, 1.4M in hexane) was added dropwise to a solution of 1-phenylsulphonylalkan-2-ols (**1**) (1 mmol) in anhydrous THF at −78 °C, and the additive added as appropriate. The mixture was stirred for 30 min, the alkyl halide was added dropwise, and the resulting solution was stirred for 30 min at −78 °C, allowed to warm to 20 °C over 2 h, and then quenched by addition of saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer was extracted twice with ethyl acetate. The organic phase was dried (Na_2SO_4), the solvents were evaporated off, and the products were isolated by column chromatography on silica gel (Wakogel C200) and/or h.p.lc.

Monodeuteriated (**1c**). The alcohol (**1c**) was used as a substrate, oil; $\nu_{max.}$ (neat) 3 500 (OH), 2 900 (CH_2), 1 320, and 1 150 cm^{-1} (SO_2); δ_H (400 MHz; $CDCl_3$) 0.87 (t, 3 H, *J* 7.02 Hz), 1.23 (br s, 16 H), 3.18 (br s, 1 H), 3.42 (s, 1 H), 4.11 (br s, 1 H), 7.56—7.69 (m, 3 H), and 7.92—7.95 (m, 2 H).

Alkylating Reagents.—3-*Phenylsulphonylbutan-2-ol* (**2a**). Mixture, viscous oil; $\nu_{max.}$(neat) 3 500 (OH), 3 100 (Ph), 1 300, and 1 150 cm^{-1} (SO_2); δ_H (100 MHz; $CDCl_3$) 1.28 (d, 3 H, *J* 6.5 Hz), 1.32 (d, 3 H, *J* 7.3 Hz), 2.9 (br s, 1 H), 3.0—3.28 (m, 2 H), 4.10—4.30 (m, 1 H), 7.56—7.69 (m, 3 H), and 7.92—8.00 (m, 2 H); *m/z* (relative intensity) 215 (*M* + 1, 2.3%), 199 (*M* − CH_3, 35%), and 170 (*M* − C_2H_4O, 100%).

3-*Phenylsulphonylpentan-2-ol* (**2b**). Mixture, viscous oil; $\nu_{max.}$(neat) 3 500 (OH), 2 950 (CH_2), 1 310, and 1 160 cm^{-1} (SO_2); δ_H (100 MHz; $CDCl_3$) 0.87 (t, 3 H, *J* 7.0 Hz), 1.24 (d, 3 H, *J* 6.6 Hz), 1.40—1.80 (m, 2 H), 2.80—3.20 (m, 1 H), 3.6 (br s, 1 H), 4.20—4.60 (m, 1 H), 7.40—7.62 (m, 3 H), and 7.80—8.00 (m, 2 H); *m/z* (relative intensity) 229 (*M* + 1, 2.4%), 213 (*M* − CH_3, 35%), and 184 (*M* − C_2H_4O, 100%).

3-*Phenylsulphonylundecan-2-ol* (**2c**). Mixture, viscous oil; $\nu_{max.}$(neat) 3 500 (OH), 2 900 (CH_2), 1 310, and 1 150 cm^{-1} (SO_2); δ_H (100 MHz; $CDCl_3$) 0.80—1.00 (m, 6 H), 1.00—1.24 (br s, 12 H), 1.60—2.00 (m, 2 H), 2.88 (t, d, 1 H, *J* 5.8 and 2.4 Hz), 3.24 (br s, 1 H), 4.20—4.52 (br s, 1 H), 7.40—7.68 (m, 1 H), and 7.68—7.96 (m, 2 H); *m/z* (relative intensity) 326 (*M*$^+$, 0.7%), 311 (*M* − CH_3, 15%), and 282 (*M* − C_2H_4O, 100%).

3-*Phenylsulphonylhex-5-en-2-ol* [erythro-(**2d**)]. Viscous oil; $\nu_{max.}$(neat) 3 500 (OH), 1 640 (CH_2=CH), 1 300, and 1 150 cm^{-1} (SO_2); δ_H(100 MHz; $CDCl_3$) 1.28 (d, 3 H, *J* 6.5 Hz), 2.57 (t, 2 H, *J* 7.1 Hz), 2.96—3.24 (br s, 1 H), 3.17 (t, d, 1 H, *J* 5.8 and 2.4 Hz), 4.20—4.48 (m, 1 H), 4.84—5.08 (m, 2 H), 5.40—5.76 (m, 1 H), 7.40—7.72 (m, 3 H), and 7.80—7.96 (m, 2 H); *m/z* (relative intensity) 241 (*M* + 1, 3.0%), 240 (*M*$^+$, 0.7%), 225 (*M* − CH_3, 2.3%), 196 (*M* − C_2H_4O, 2.4%), and 98 (*M* − $PhSO_2H$, 100%). Compound *threo*-(**2d**), δ_H (100 MHz; $CDCl_3$) 1.28 (d, 3 H, *J* 6.6 Hz), 2.53 (t, 2 H, *J* 7.3 Hz), 2.96—3.24 (br s, 1 H), 3.22 (t, d, 1 H, *J* 6.1 and 6.1 Hz), 4.20—4.48 (m, 1 H), 4.84—5.08 (m, 2 H), 5.40—5.76 (m, 1 H), 7.40—7.73 (m, 3 H), and 7.80—7.96 (m, 2 H).

6-*Methyl*-3-*phenylsulphonylhept-5-en-2-ol* (**2e**). Mixture, viscous oil; $\nu_{max.}$(neat) 3 500 (OH), 2 900 (CH_2), 1 640 (CH_2=CH), 1 310, and 1 160 cm^{-1} (SO_2); δ_H(100 MHz; $CDCl_3$) 1.32 (d, 3 H, *J* 6.9 Hz), 1.52 (d, 6 H, *J* 5.9 Hz), 2.50 (t, 2 H, *J* 6.6 Hz), 3.00 (t, d, 1 H, *J* 5.8 and 2.4 Hz), 3.16 (br s, 1 H), 4.20—4.60 (m, 1 H), 4.80—5.00 (m, 1 H), 7.40—7.66 (m, 3 H), and 7.80—8.00 (m, 2 H); *m/z* (relative intensity) 269 (*M* + 1, 3%), 268 (*M*$^+$, 0.6%), 253 (*M* − CH_3, 2.4%), 224 (*M* − C_2H_4O, 2.5%), and 154 (*M* − $PhSO_2H$, 100%).

5-*Methyl*-2-*phenylsulphonylhexan-3-ol* [erythro-(**2f**)]. Viscous oil; $\nu_{max.}$(neat) 3 500 (OH), 2 950 (CH_2), 1 300, and 1 160 cm^{-1} (SO_2); δ_H(400 MHz; $CDCl_3$) 0.817 (d, 3 H, *J* 6.71 Hz), 0.854 (d, 3 H, *J* 6.72), 1.313 (d, 3 H, *J* 7.01 Hz), 1.513—1.585 (m, 2 H), 1.652—1.721 (m, 1 H), 2.870 (br s, 1 H), 3.006 (q, d, 1 H, *J* 7.02 and 1.22 Hz), 4.119 (q, *J* 7.02 Hz, 1 H), 7.571—7.708 (m, 3 H), and 7.890—7.927 (m, 2 H); *m/z* (relative intensity) 257 (*M* + 1, 1.4%), 256 (*M*$^+$, 2.3%), 199 (M − C_4H_9, 17%), and 170 (*M* − $C_5H_{10}O$, 100%). Compound *threo*-(**2f**), δ_H(400 MHz; $CDCl_3$) 0.900 (d, 3 H, *J* 6.41 Hz), 0.932 (d, 3 H, *J* 7.32 Hz), 1.156 (d, 3 H, *J* 7.32 Hz), 1.235—1.321 (m, 2 H), 1.451—1.489 (m, 1 H), 3.096—3.208 (m, 1 H), 3.682 (br s, 1 H), 4.092—4.145 (m, 1 H), 7.556—7.707 (m, 3 H), and 7.893—7.921 (m, 2 H).

2-*Methyl*-5-*phenylsulphonyloct-7-en-4-ol* [erythro-(**2g**)]. Viscous oil; $\nu_{max.}$(neat) 3 500 (OH), 3 100 (Ph), 2 900 (CH_2), 1 640 (olefin), 1 300, and 1 150 cm^{-1} (SO_2); δ_H (100 MHz; $CDCl_3$) 0.62—1.02 (m, 6 H), 1.02—1.40 (m, 1 H), 1.4—1.96 (m, 2 H), 2.56 (t, 2 H, *J* 7.3 Hz), 2.96—3.22 (br s, 1 H), 3.15 (t, d, 1 H, *J* 5.8 and 2.4 Hz), 4.20—4.48 (br s, 1 H), 4.84—5.20 (m, 2 H), 5.48—5.92 (m, 1 H), 7.48—7.80 (m, 3 H), and 7.80—8.08 (m, 2 H); *m/z* (relative intensity) 283 (*M* + 1, 2.9%), 282 (*M*$^+$, 0.6%), 225 (*M* − C_4H_9, 3.0%), 196 (*M* − $C_5H_{10}O$, 3.2%), and 140 (*M* − $PhSO_2H$, 100%). Compound *threo*-(**2g**), δ_H(100 MHz; $CDCl_3$) 0.62—1.00 (m, 6 H), 1.00—1.38 (m, 1 H), 1.40—1.96 (m, 2 H), 2.48 (t, 2 H, *J* 7.2 Hz), 3.00—3.25 (br s, 1 H), 3.25 (t, d, 1 H, *J* 6.1 and 6.1 Hz), 4.20—4.50 (br s, 1 H), 4.84—5.20 (m, 2 H),

5.48—6.00 (m, 1 H), 7.48—7.80 (m, 3 H), and 7.80—8.00 (m, 2 H).

3-*Phenylsulphonyldodecan*-2-*ol* [erythro-(**2h**)]. Viscous oil; $\nu_{max.}$(neat) 3 500 (OH), 2 950 (CH_2), 1 310, and 1 150 cm^{-1} (SO_2); δ_H(400 MHz; $CDCl_3$) 0.874 (t, 3 H, *J* 7.02 Hz), 1.316 (d, 3 H, *J* 7.02 Hz), 1.224—1.626 (m, 16 H), 2.906 (br s, 1 H), 3.037 (q, d, 1 H, *J* 7.02 and 1.22 Hz), 4.243 (q, 1 H, *J* 3.97 Hz), 7.573—7.707 (m, 3 H), and 7.893—7.916 (m, 2 H); *m*/*z* (relative intensity) 326 (M^+, 0.7%), 199 ($M - C_9H_{19}$, 12%), and 170 ($M - C_{10}H_{20}O$, 100%). Compound *threo*-(**2h**), δ_H(400 MHz; $CDCl_3$) 0.874 (t, 3 H, *J* 7.02 Hz), 1.156 (d, 3 H, *J* 7.02 Hz), 1.256—1.617 (m, 16 H), 3.186 (q, d, 1 H, *J* 7.33 and 7.02 Hz), 3.822 (br s, 1 H), 3.997—4.037 (m, 1 H), 7.569—7.701 (m, 3 H), and 7.894—7.918 (m, 2 H).

5-*Phenylsulphonyltetradec*-1-*en*-4-*ol* [erythro-(**2i**)]. Viscous oil; $\nu_{max.}$(neat) 3 500 (OH), 2 920 (CH_2), 1 640 (olefin), 1 310, and 1 160 cm^{-1} (SO_2); δ_H (400 MHz; $CDCl_3$) 0.87 (t, 3 H, *J* 7.02 Hz), 1.22 (br s, 16 H), 2.61—2.69 (m, 2 H), 3.15—3.19 (br s, 1 H), 3.17 (t, d, 1 H, *J* 5.80 and 2.44 Hz), 4.02—4.32 (m, 1 H), 4.92—5.16 (m, 2 H), 5.52—5.92 (m, 1 H), 7.42—7.72 (m, 3 H), and 7.72—8.02 (m, 2 H); *m*/*z* (relative intensity) 353 (M + 1, 2.8%), 352 (M^+, 0.8%), 225 ($M - C_9H_{19}$, 2.3%), and 210 (M − $PhSO_2H$, 100%). Compound *threo*-(**2i**), δ_H(400 MHz; $CDCl_3$) 0.87 (t, 3 H, *J* 7.02 Hz), 1.25 (m, 16 H), 2.41—2.51 (m, 2 H), 3.20—3.25 (br s, 1 H), 3.22 (t, d, 1 H, *J* 6.10 Hz), 4.02—4.42 (m, 1 H), 4.92—5.16 (m, 2 H), 5.52—5.92 (m, 1 H), 7.42—7.72 (m, 3 H), and 7.72—8.03 (m, 2 H).

4-*Phenyl*-3-*phenylsulphonylbutan*-2-*ol* [erythro-(**2j**)]. Viscous oil; $\nu_{max.}$(neat) 3 500 (OH), 3 000 (CH_2), 1 460, 1 310, and 1 160 cm^{-1} (SO_2); δ_H(400 MHz; $CDCl_3$) 1.383 (d, *J* 7.02 Hz, 3 H), 2.429—2.642 (m, 2 H), 2.80 (br s, 1 H), 3.102 (q, 1 H, *J* 7.33 Hz), 4.101 (q, 1 H, *J* 7.02 Hz), and 7.109—7.912 (m, 10 H); *m*/*z* (relative intensity) 291 (M + 1, 0.4%), 290 (M^+, 0.2%), 199 ($M - PhCH_2$, 100%), and 170 ($M - PhCH_2CHO$, 22%). Compound *threo*-(**6j**) , δ_H(400 MHz; $CDCl_3$) 1.289 (d, 3 H, *J* 7.02 Hz), 2.622—2.700 (m, 2 H), 3.271 (q, d, 1 H, *J* 7.33 and 7.02 Hz), and 7.190—7.916 (m, 10 H).

1-*Phenyl*-2-*phenylsulphonylhex*-5-*en*-3-*ol* [erythro-(**2k**)]. Viscous oil; $\nu_{max.}$(neat) 3 500 (OH), 3 100 (Ph), 1 640 (olefin), 1 320, and 1 160 cm^{-1} (SO_2); δ_H(100 MHz; $CDCl_3$) 2.50—2.70 (m, 4 H), 3.15—3.19 (br s, 1 H), 3.17 (t, d, 1 H, *J* 5.8 and 2.4 Hz), 4.02—4.42 (br s, 1 H), 4.92—5.16 (m, 2 H), 5.52—5.92 (m, 1 H), and 7.19—8.00 (m, 10 H); *m*/*z* (relative intensity) 317 (M + 1, 2.8%), 225 ($M - PhCH_2$, 2.8%), and 196 ($M - PhSO_2H$, 100%).

General Procedure for the Reaction of the Dianion with Aldehydes.—The aldehyde (1.1 equiv.) was added at −78 °C to the solution of dianion, prepared by the same method as in the alkylation reaction. After being stirred for 30 min at −78 °C the reaction was quenched by addition of saturated aqueous NH_4Cl. The products were isolated by a similar work-up to that previously used.

3-*Phenylsulphonyltridecane*-2,4-*diol* (**3a**). Mixture, viscous oil; $\nu_{max.}$(neat) 3 500 (OH), 2 900 (CH_2), 1 590, 1 310, and 1 150 cm^{-1} (SO_2); δ_H(100 MHz; $CDCl_3$) 0.88 (t, 3 H, *J* 7.0 Hz), 1.00—1.80 (m, 19 H), 3.08—3.20 (m, 1 H), 3.40—3.80 (br s, 2 H), 4.00—4.60 (m, 2 H), 7.40—7.76 (m, 3 H), and 7.78—8.00 (m, 2 H); *m*/*z* (relative intensity) 357 (M + 1, 1%), 229 ($M - C_9H_{19}$, 100%), and 141 ($PhSO_2$, 90%).

3-*Phenylsulphonylpentadecane*-2,4-*diol* (**3b**). Major isomer, Viscous oil; $\nu_{max.}$(neat) 3 500 (OH), 2 900 (CH_2), 1 590, 1 320, and 1 150 cm^{-1} (SO_2); δ_H (100 MHz; $CDCl_3$) 0.88 (t, 3 H, *J* 7.0 Hz), 1.00—1.80 (m, 23 H), 3.06—3.20 (m, 1 H), 3.40—3.80 (br s, 2 H), 4.00—4.60 (m, 2 H), 7.40—7.76 (m, 3 H), and 7.78—8.00 (m, 2 H); *m*/*z* (relative intensity) 385 (M + 1, 0.8%), 229 ($M - C_{11}H_{23}$, 100%), and 141 ($PhSO_2$, 98%). Compound (**3b**) (minor isomer), δ_H (100 MHz; $CDCl_3$) 0.88 (t, 3 H, *J* 7.0 Hz), 1.00—1.80 (m, 23 H), 3.08—3.24 (m, 1 H), 3.40—3.80 (br s, 2 H), 4.00—4.60 (m, 2 H), 7.40—7.76 (m, 3 H), and 7.78—8.00 (m, 2 H).

6,10-*Dimethyl*-3-*phenylsulphonylundec*-9-*ene*-2,4-*diol* (**3c**). Mixture, viscous oil; $\nu_{max.}$(neat) 3 500 (OH), 2 950 (CH_2), 1 320, and 1 160 cm^{-1} (SO_2); δ_H(100 MHz; $CDCl_3$) 0.82 (d, 3 H, *J* 6.6 Hz), 1.00—2.00 (m, 19 H), 3.08—3.20 (m, 1 H), 3.40—3.80 (br s, 2 H), 4.00—4.60 (m, 2 H), 5.00 (t, 1 H, *J* 6.6 Hz), 7.40—7.76 (m, 3 H), and 7.78—8.00 (m, 2 H); *m*/*z* (relative intensity) 355 (M + 1, 1%), 229 ($M - C_9H_{17}$, 100%), and 141 ($PhSO_2$, 90%).

2-*Methyl*-5-*phenylsulphonylpentadecane*-4,6-*diol* (**3d**). Mixture, viscous oil; $\nu_{max.}$(neat) 3 500 (OH), 2 900 (CH_2), 1 310, and 1 160 cm^{-1} (SO_2); δ_H(100 MHz; $CDCl_3$) 0.76—1.00 (m, 9 H), 1.00—1.80 (m, 18 H), 3.08 (m, 1 H), 3.70 (br s, 2 H), 4.06—4.48 (m, 2 H), 7.40—7.68 (m, 3 H), and 7.68—7.96 (m, 2 H); *m*/*z* (relative intensity) 399 (M + 1, 1%), 271 ($M - C_9H_{19}$, 100%), and 141 ($PhSO_2$, 95%).

2-*Methyl*-5-*phenylsulphonylheptadecane*-4,6-*diol* (**3e**). Mixture, viscous oil; $\nu_{max.}$(neat) 3 500 (OH), 2 900 (CH_2), 1 310, and 1 150 cm^{-1} (SO_2); δ_H(100 MHz; $CDCl_3$) 0.76—1.00 (m, 9 H), 1.00—1.80 (m, 22 H), 3.08 (m, 1 H), 3.70 (br s, 2 H), 4.06—4.48 (m, 2 H), 7.40—7.68 (m, 3 H), and 7.68—7.96 (m, 2 H); *m*/*z* (relative intensity) 413 (M + 1, 1%), 271 ($M - C_{11}H_{23}$, 90%), and 141 ($PhSO_2$, 100%).

2,8,12-*Trimethyl*-5-*phenylsulphonyltridec*-11-*ene*-4,6-*diol* (**3f**). Mixture, viscous oil; $\nu_{max.}$(neat) 3 500 (OH), 2 900 (CH_2), 1 320, and 1 150 cm^{-1} (SO_2); δ_H(100 MHz; $CDCl_3$) 0.76—1.00 (m, 9 H), 1.00—2.00 (m, 17 H), 3.08 (m, 1 H), 3.70 (br s, 2 H), 4.06—4.48 (m, 2 H), 5.00 (t, 1 H, *J* 6.6 Hz), 7.40—7.68 (m, 3 H), and 7.68—7.96 (m, 2 H); *m*/*z* (relative intensity) 397 (M + 1, 1%), 271 ($M - C_9H_{17}$, 100%), and 141 ($PhSO_2$, 95%).

5-*Phenylsulphonylpentadecane*-4,6-*diol* (**3g**). Major isomer, viscous oil; $\nu_{max.}$(neat) 3 500 (OH), 2 900 (CH_2), 1 310br, and 1 150br cm^{-1} (SO_2); δ_H(100 MHz; $CDCl_3$) 0.66—1.06 (m, 6 H), 1.06—2.00 (m, 20 H), 3.06—3.20 (m, 1 H), 3.66 (m, 2 H), 4.06—4.46 (m, 2 H), 7.40—7.80 (m, 3 H), and 7.80—8.00 (m, 2 H); *m*/*z* (relative intensity) 271 ($M - C_9H_{19}$, 90%) and 141 ($PhSO_2$, 100%). Compound (**3g**) (minor isomer), δ_H(100 MHz; $CDCl_3$) 0.70—1.00 (m, 6 H), 1.00—1.86 (m, 20 H), 3.08—3.24 (m, 1 H), 3.24—3.72 (br s, 2 H), 4.00—4.40 (m, 2 H), 7.40—7.78 (m, 3 H), and 7.78—8.00 (m, 2 H).

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