Nickel-catalysed Substitutions of Aryl *tert*-Butyl Sulfones with Organometallic Reagents: Synthesis of *ortho*-Substituted Unsymmetrical Biaryls

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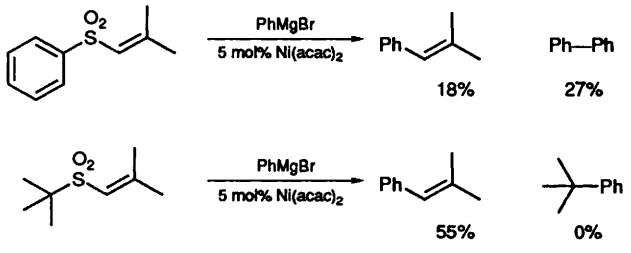
In the presence of a catalytic amount of a nickel salt, aryl *tert*-butyl sulfones react with aryl Grignard reagents to give biaryls. This reaction is used in conjunction with the powerful *ortho*-lithiation-directing ability of aryl *tert*-butyl sulfonyl groups to make unsymmetrical *ortho*-substituted biaryls. In certain cases, the substitution of an aryl alkylsulfonyl group by an organometallic reagent is possible without a transition metal catalyst.

The value of sulfones to the synthetic chemist owes much to the great variety of reactions that molecules containing sulfonyl groups can undergo.[1] Alkyl- and aryl-sulfonyl groups are easy to introduce into organic molecules, though once the required transformation has been performed, their removal sometimes causes problems. Traditionally, sulfonyl groups have been removed by reduction (for example, with alkali metals[2] and their amalgams,[3] or with Raney nickel[4]), which simply replaces the sulfonyl group with a hydrogen atom, or by base catalysed[5] or reductive[6] eliminations, which leave behind a double bond. More constructive desulfonylations rely on transition metal-catalysed nucleophilic substitution of sulfinate from a (usually allylic[7,8] or vinylic[9]) sulfone. Recently, we reported two methods[10,11] for the transformation of allylic sulfones into organometallic nucleophiles, one using palladium and zinc,[10] and the other using samarium(II).[11] We now report[12] a new method for the nucleophilic substitution of sulfonyl groups attached to aromatic rings, and we demonstrate the use of this reaction in conjunction with the powerful *ortho*-lithiation-directing ability of aryl *tert*-butyl sulfonyl groups[13] to make unsymmetrical *ortho*-substituted biaryls.

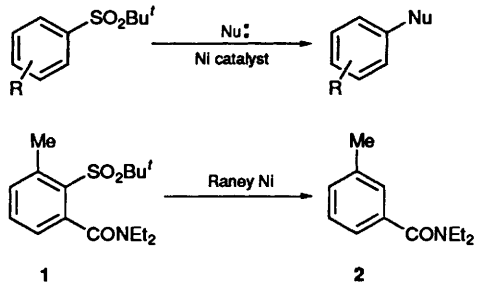
During previous work on the nucleophilic substitution of vinylic aryl sulfones with Grignard reagents under transition metal catalysis,[9] we had noticed that nickel catalysts were capable not only of catalysing cleavage of the vinyl sp^2 C–S bond, but also of the aryl sp^2 C–S bond (Scheme 1). The sp^3



Scheme 1

C–S bond of a *tert*-butyl sulfone was, however, never cleaved by nickel. In the light of these results, it was clearly possible that nickel salts might catalyse the displacement of a *tert*-butylsulfonyl group attached to an aromatic nucleus (Scheme 2). Wenkert[14] had already shown that nickel salts catalyse the substitution of aryl alkyl sulfides by Grignard reagents.[15]

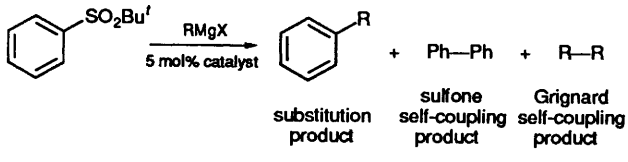
A substitution reaction of an aryl *tert*-butyl sulfone would be a valuable synthetic method, since Snieckus[13] has



Scheme 2

demonstrated that the *tert*-butylsulfonyl group is an extremely powerful director of *ortho*-lithiation, making a range of substituted aryl *tert*-butyl sulfones readily available. Snieckus's only attempt to remove the sulfonyl group from a substituted aryl *tert*-butyl sulfone **1** used Raney nickel to give a moderate yield of the *meta* substituted **2**. It would be very useful to be able to replace the alkylsulfonyl group with a group other than just a hydrogen atom.

Metal-catalysed Substitution Reactions of Aryl tert-*Butyl Sulfones.*—In our initial investigations, we treated a solution of phenyl *tert*-butyl sulfone with 5 mol% of a catalyst and an excess of a Grignard reagent, in the manner of ref. 9 (Scheme 3). After



Scheme 3

the brown mixture had been stirred for 24 h at 20 °C under nitrogen, the reaction was quenched with aqueous ammonium chloride, and the yield of the various products was determined by GC with an internal standard, calibrated against authentic samples. Table 1 shows the results of this reaction for a variety of catalysts (entries 1–5) and Grignard reagents (entries 5–11). It was immediately obvious that the nickel catalysts performed much better than the one iron catalyst tried (entry 1), and that the best catalysts for the reaction were $NiCl_2(PPh_3)_2$ (entry 2) and $Ni(acac)_2$ (entry 5). For both of these catalysts, starting material was all consumed within 3 h at room temperature, and excellent yields of the substitution product were observed. No substitution was observed in the absence of a catalyst. In most cases, two by-products were observed: biphenyl, which arises from self-coupling of the sulfone (and whose formation therefore reduces the yield of the desired substitution product)

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Table 1 Catalysed reactions of *tert*-butyl phenyl sulfone with Grignard reagents

Entry	RMgX	Equiv.	Catalyst	Substitution (%)[a]	Sulfone self-coupling (%)[a]	Starting material (%)[a]	Grignard self-coupling (%)[a,b]
1	*p*-TolMgBr*	2	$Fe(acac)_3$	<2	<4	98	42
2	*p*-TolMgBr	2	$NiCl_2(PPh_3)_2$	88	15	3	57
3	*p*-TolMgBr	2	$NiCl_2$(dppe)[c]	57	14	5	48
4	*p*-TolMgBr	2	$NiCl_2$(dppb)[d]	56	21	0	47
5	*p*-TolMgBr	2	$Ni(acac)_2$	80	15	0	40
6	*o*-TolMgBr	2	$Ni(acac)_2$	82	4	0	30
7	MeMgCl	2	$Ni(acac)_2$	<4	0	68	—
8	MeMgCl	4	$Ni(acac)_2$	13	10	27	—
9	BuMgCl	2	$Ni(acac)_2$	1	22	1	1
10	BuMgCl	4	$Ni(acac)_2$	2	15	1	1
11	BuMgCl	4	$NiCl_2$(dppp)[e]	9	12	2	1
12	*p*-TolMgBr	1	$NiCl_2(PPh_3)_2$	<1	0	66	9
13	*p*-TolMgBr	1	$NiCl_2$(dppe)[c]	7	<1	59	16
14	*p*-TolMgBr	1	$Ni(acac)_2$	20	<1	47	0
15	*p*-TolMgBr	1.2	$Ni(acac)_2$	53	29	19	55

* Tol = MeC_6H_4. [a] Determined by GC. [b] Corrected for the small amount already present in the Grignard reagent. [c] dppe = bis(diphenylphosphino)ethane. [d] dppb = bis(diphenylphosphino)butane. [e] dppp = bis(diphenylphosphino)propane.

and a symmetrical biaryl or octane, from self-coupling (oxidation) of the excess Grignard reagent.

The reaction was highly dependent on the nature of the Grignard reagent (entries 5–11). With aryl Grignards (entries 5 and 6), excellent yields of substitution products were observed, but with methyl Grignard (even with 4 equiv.) large quantities of starting material remained (entries 7 and 8). With butyl Grignard (entries 9–11), starting material was consumed, but not in the desired substitution: we believe that Grignard reagents bearing β-hydrogen atoms reduce the sulfone to benzene (see below).

In an attempt to suppress these side-reactions, some experiments were performed with just 1 equiv. of the Grignard reagent (entries 12–14). $Ni(acac)_2$ performed best under these conditions but, nonetheless, the yield of substitution product was very low, with large quantities of starting material remaining. Using just a slight excess of Grignard reagent increased the yield of the substitution product to over 50%, but also gave large amounts of the sulfone self-coupled by-product (entry 15). Other modifications to the conditions (performing the reaction at 0 °C or at reflux, for example) had no beneficial effect on the yield, and from this set of experiments we concluded that substitutions of aryl *tert*-butyl sulfones are possible using aryl Grignard reagents with nickel catalysts, and that the best yields are obtained with a considerable excess (2 equiv.) of Grignard reagent in the presence of $Ni(acac)_2$ or $NiCl_2(PPh_3)_2$.

The reaction between an aryl *tert*-butyl sulfone and an aryl Grignard reagent is analogous to the well-known couplings of aryl halides with aryl organometallics under nickel or palladium catalysis,[16] and we assume that the same mechanism (that proposed by Kumada[17]) operates. A small amount of nickel(0), the true catalyst, is produced from the nickel(II) catalyst, probably by transmetallation with two Grignard molecules and reductive elimination to form the biaryl. The nickel(0) inserts into the sp^2 C–S bond of the aryl sulfone, and the resulting arylnickel(II) sulfonate complex[18] undergoes ligand exchange with a molecule of Grignard reagent, giving an unsymmetrical bis(aryl) complex. Reductive elimination completes the cycle, giving the substitution product and reproducing the nickel(0).

The by-products, self-coupled sulfone and an equimolar amount of self-coupled Grignard reagent, may be produced by ligand exchange between two of the unsymmetrical bis(aryl) nickel(II) complexes to give the two symmetrical bis(aryl) nickel(II) complexes from which the biaryls form by reductive elimination of the metal.† However, far more self-coupled Grignard reagent is produced in these reactions than can arise by this mechanism. The Grignard self-coupling reaction is an oxidation, and a small amount is formed by reduction of the nickel(II) to nickel(0) in the initiation step of the catalytic cycle. However, another oxidising agent is clearly required to account for the quantities produced in the reaction. It is possible that the sulfinate anions produced in the reaction fulfil this role.[19]

Synthesis of Unsymmetrical ortho-*Substituted Biaryls.*— Biaryls are important molecules. They occur widely in both natural and synthetic chemistry, for example as drugs[20] or as interesting and powerful chiral catalysts.[21] Much effort has therefore been directed towards methods for making them.[22] The classical Ullman reaction,[23] a copper-catalysed coupling of aryl halides, and Semmelhack's milder nickel variant,[24] give symmetrical biaryls, as do 'biomimetic' methods based on the coupling of phenolic radicals.[25] However, methods leading to unsymmetrical biaryls are more valuable. Such reactions involve either the coupling of two electronically or functionally different aryl subunits,[22,26] or the coupling of two aryl subunits intramolecularly.[22,27]

The most widely used methods for making unsymmetrical biaryls are found among the first of these two classes of reactions, which is clearly the more versatile. These include the coupling of aryl Grignard reagents, arylcoppers,[26,28] or arylzincs[29] with aryl halides,[30] often catalysed by nickel[18] or palladium,[31] and the Suzuki coupling[32] of arylboronic acids with aryl halides in the presence of a palladium catalyst. The latter has been extensively investigated and developed by Snieckus.[33] Meyers[34] has developed an alternative route based on the aromatic nucleophilic substitution of methoxy groups *ortho* to an oxazoline substituent.

As Snieckus has shown, the *tert*-butylsulfonyl group can be used to introduce a variety of *ortho* substituents. Alternatively, lithiation of an aromatic nucleus, followed by di-*tert*-butyl disulfide quench and oxidation to the sulfone, gives other *ortho*-substituted aryl *tert*-butyl sulfones (Scheme 4). We used these methods to make the *ortho*-substituted aryl *tert*-butyl sulfones **3** shown in Table 2. The sulfones were treated with aryl Grignard reagents and a nickel catalyst under conditions similar to those

† Very little self-coupled sulfone is obtained from the reaction with *o*-tolylmagnesium bromide, in which crowding between the two *ortho* substituents would be expected to disfavour this exchange.

Table 2 Nickel-catalysed substitutions of substituted aryl *tert*-butyl sulfones

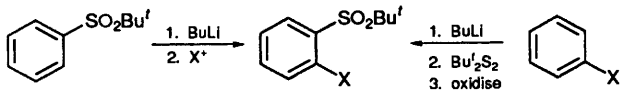
Entry	SM[a]	X	Y	Z	R	Equiv.	Cat.[b]	*t*/h	**4** (%)[c,d]	**5** (%)[c]	**6** (%)[c]	SM[a] (%)[c]
1	**3a**	Me	H	H	Ph	4	A	3	66	12	12	0
2	**3a**	Me	H	H	Ph	2	B	3	77	—	6	8
3	**3b**	$SiMe_3$	H	H	*p*-Tol*	4	A	24	67	27	0	0
4	**3b**	$SiMe_3$	H	H	*p*-Tol	2	A	2.5	84	—	0	21
5	**3b**	$SiMe_3$	H	H	*p*-Tol	2	B	3	61	—	0	0
6	**3c**	$CH{=}CH_2$	H	H	*p*-Tol	2	B	2.5	36	—	0	21
7	**3d**	*e*	H	H	*p*-Tol	4	A	3	36	25	0	20
8	**3e**	$CONPr^i_2$	H	H	Ph	4	A	24	95 (81, **4a**)	2	0	0
9	**3e**	$CONPr^i_2$	H	H	Ph	2	A	24	66 (53, **4a**)	2	0	25
10	**3e**	$CONPr^i_2$	H	H	*p*-Tol	4	A	24	92 (86, **4b**)	2	0	0
11	**3e**	$CONPr^i_2$	H	H	*o*-Tol	2	A	24	35	40	0	0
12	**3e**	$CONPr^i_2$	H	H	*o*-Tol	4	A	66	58 (42, **4c**)	41	0	1
13	**3f**	OMe	H	H	Ph	4	A	3	38	16	24	5
14	**3f**	OMe	H	H	*p*-Tol	4	A	24	33	31	15	17
15	**3f**	OMe	H	H	*p*-Tol	2	B	6	(51, **4d**)	—	5	3
16	**3f**	OMe	H	H	*p*-Tol	2	C	2	(55, **4d**)	—	3	0
17	**3g**	$CONPr^i_2$	Me	H	*p*-Tol	6[f]	A	24	48 (47, **4e**)	5	0	41
18	**3h**	OMe	Me	H	*p*-Tol	4	A	24	20	53	0	16
19	**3i**	H	H	OMe	*p*-Tol	2	A	3	(59, **4f**)	—	4	9
20	**3i**	H	H	OMe	*p*-Tol	2	B	3	35	—	11	4

* Tol = MeC_6H_4. [a] SM = starting material. [b] Catalyst: A = $Ni(acac)_2$; B = $NiCl_2(PPh_3)_2$; C = $Ni(PPh_3)_4$. [c] Determined by GC. [d] Isolated yields and compound numbers in parentheses. [e] *m*-$MeOC_6H_4(MeO)CH$. [f] Reaction carried out at 40 °C.

Table 3 Reduction of aryl *tert*-butyl sulfones by isopropylmagnesium chloride

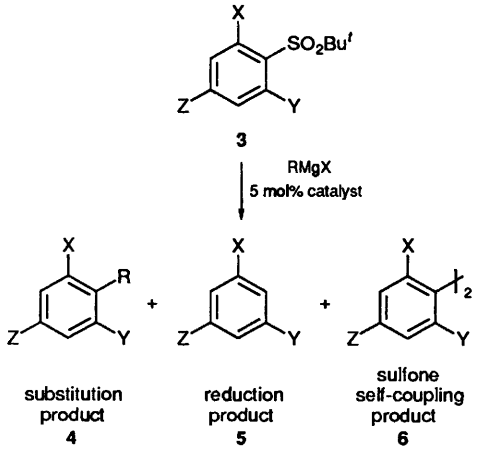
Entry	Starting material	X	Y	Z	**5** (%)[a]
1	**3e**	$CONPr^i_2$	H	H	89 (81)
2	**3g**	$CONPr^i_2$	Me	H	60
3	**3h**	OMe	Me	H	96 (92)

[a] Determined by GC; isolated yields in parentheses.



Scheme 4

optimised for reactions of the parent *tert*-butyl phenyl sulfone (Scheme 5). The results of these reactions are summarised in Table 2.



Scheme 5

The yields of the desired substitution products **4** were heavily dependent on the starting materials. The amides **3e** (entries 8 and 10) gave the best yields (almost quantitative), but **3a** and **b** (entries 1–5) also performed well. The methyl ethers **3d**, **f** and **i** (entries 7, 13–16, 19 and 20) and the allyl-substituted **3c** (entry 6) gave only poor yields of the substitution product, possibly because of coordination to nickel.

In some cases, the yield also depended significantly on which of the two catalysts, $Ni(acac)_2$ or $NiCl_2(PPh_3)_4$, was used (compare entries 4 and 5, 14 and 15, 19 and 20). In one reaction, $Ni(PPh_3)_4$ was used as a catalyst, prepared *in situ* by the method of Negishi,[35] but the results did not differ significantly from those obtained with $NiCl_2(PPh_3)_4$ (entry 16).

In most cases, the *ortho* substituent completely suppressed self-coupling of the sulfone, but in some cases reduction (substitution of the sulfonyl group for hydrogen) was an important side-reaction. This was true for the hindered 2,6-disubstituted sulfone **3g** (entry 17), and for reactions with *o*-tolyl Grignard reagents (entries 11 and 12).

In some cases, high yields were obtained with just 2 equiv. of Grignard reagent, while in others, 4 equiv. were necessary for complete consumption of the starting material. For the very hindered sulfone **3g**, the best yields were obtained by carrying out the reaction with 6 equiv. of Grignard reagent at 40 °C for 24 h (entry 17).

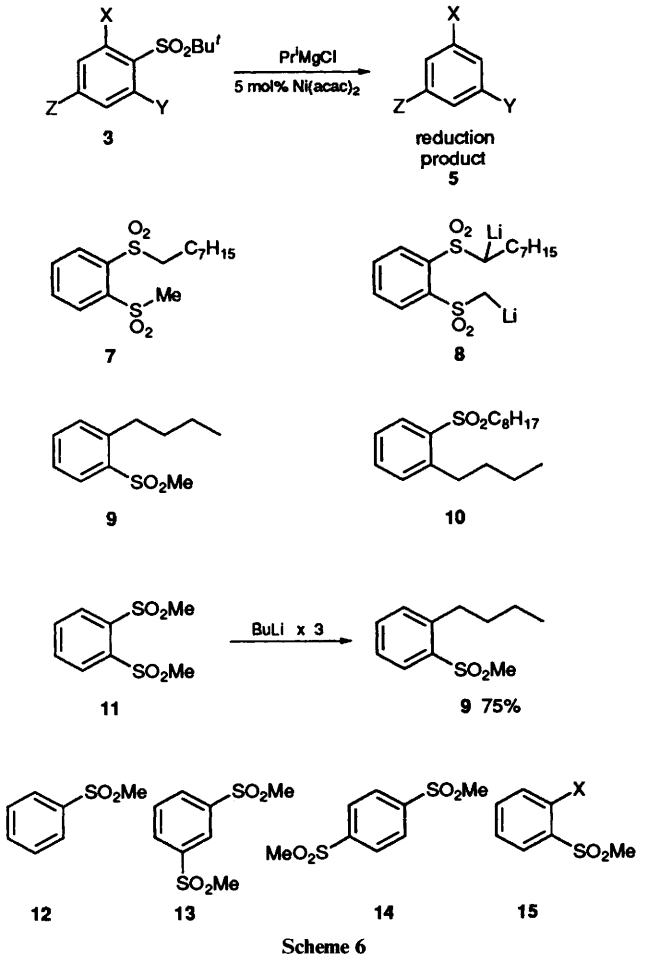
Negishi[35] has shown that arylzincs often perform better in coupling reactions with aryl halides than their Grignard counterparts. With our sulfones, however, arylzincs proved unreactive.

Nickel-catalysed Reduction of Aryl tert-*Butyl Sulfones.*—The synthetic method we propose here uses the sulfonyl group as a latent aryl substituent, into which it is converted once construction of the polyaromatic system, using its directing properties, is complete. It is also useful to be able to use the sulfonyl group as a latent hydrogen atom, by using the properties of the sulfone and then reducing the C–S bond.

By using isopropylmagnesium chloride as a reducing agent,[14a] we were able to make this reduction pathway the major course of the reaction. Table 3 shows the results of treating some sulfones with isopropylmagnesium chloride in the presence of nickel(II) acetoacetonate. In all cases, high yields of the reduced product **5** were obtained. These products are particularly interesting if, like **5b**, they are *meta*-substituted,

with the *meta* relationship having been controlled by two *ortho*-lithiation steps.

Uncatalysed Substitutions.—During some attempts to lithiate the sulfone **7**, we discovered that 2 equiv. of butyllithium not only gave the dilithiated product **8**, but could also substitute one of the alkylsulfonyl groups with a butyl group to give a mixture of the sulfones **9** and **10** (Scheme 6). With 3 equiv. BuLi,

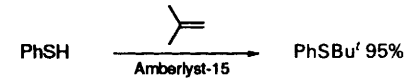


Scheme 6

the sulfone **11** gave the butylated **9** in 75% yield after 24 h at room temperature. This reaction worked only with 1,2-bis(sulfonyl)-benzenes: the methyl phenyl sulfone **12** and the 1,3- and 1,4-bis(sulfonyl)benzenes **13** and **14** did not undergo substitution. This reaction is similar in outline to the substitutions we have just described: an organometallic reagent substitutes an alkylsulfonyl group from a benzene nucleus, though no catalyst is necessary. Unfortunately, attempts to substitute alkylsulfonyl groups from other 1,2-disubstituted benzenes **14** (X = OMe, Cl, $CONPr^i_2$) were unsuccessful.

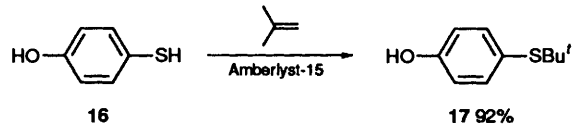
Nucleophilic aromatic substitutions directed by an *ortho* oxazolinyl group have been extensively studied by Meyers,[34] and Flippin[36] has reported a similar reaction of *ortho*-substituted imines. Our particular reaction may have mechanistic characteristics in common with these reactions (for example, pre-coordination between the sulfonyl groups and the butyllithium may be important), and it is also related to the aromatic substitution reaction of *tert*-butyl phenyl sulfones with butyllithium described by Stoyanovich.[37] Its apparent lack of generality meant that this reaction was not studied further.

Synthesis of the Starting Materials.—We found Snieckus's method[13] for the synthesis of *tert*-butyl phenyl sulfone (attack of phenyllithium on di-*tert*-butyl disulfide, followed by oxidation to the sulfone) to suffer from a number of drawbacks: the starting materials are relatively expensive, the reaction is rather unreliable, and 1 equiv. of foul-smelling 2-methylpropane-2-thiol is produced as a by-product. A modification of Alexakis's method[38] for the *tert*-butylation of alcohols on the other hand provided a cheap, more convenient, and more pleasant way to make *tert*-butyl phenyl sulfide. Benzenethiol was treated with isobutene in the presence of Amberlyst 15 to give a 95% yield of the sulfide (Scheme 7). Oxidation by the



Scheme 7

method of McKillop[39] gave the sulfone. Butylation of the hydroxy thiol **16** by this method gave mainly monobutylated **17** (Scheme 8), which was subsequently methylated and oxidised to give the sulfone **3i**.



Scheme 8

The anisole **3e** and the amide **3f** were made by quenching lithiated anisole or *N*,*N*-diisopropylbenzamide with di-*tert*-butyl disulfide, followed by oxidation. The other compounds **3** were all made according to Snieckus's method[13] for the *ortho*-functionalisation of aryl *tert*-butyl sulfones.

The aryl methyl sulfones **7** and **11–14** were made from 1,2-dichlorobenzene by Tiecco's[40] nucleophilic substitution method or by methylation and oxidation of thiols.

Experimental

General.—Flash column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh). Thin layer chromatography (TLC) was carried out on commercially available precoated plates (Merck silica Kieselgel $60F_{254}$). All solvents were distilled before use. Tetrahydrofuran was freshly distilled from potassium using benzophenone radical as an indicator. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker WM 200 or WM 250 spectrometers. Chemical shifts are quoted in parts per million downfield of tetramethylsilane. *J* Values are given in Hz. Mass spectra were recorded by Chemical Ionisation (CI). Microanalyses were carried out by the staff of l'Université Pierre et Marie Curie, place Jussieu, Paris.

tert-*Butyl Phenyl Sulfone.*—A large excess of isobutene was condensed into a rapidly stirred suspension of Amberlyst H-15 (3 g) in benzenethiol (11 g, 0.1 mol) and diethyl ether (80 cm^3) at −78 °C. The suspension was allowed to warm to room temperature over 72 h, and then filtered. The solvent was removed under reduced pressure and the residue distilled to give *tert*-butyl phenyl sulfide[13] (16.3 g, 95%), b.p. 79–80 °C (10 mmHg).

Sodium perborate tetrahydrate (20.8 g, 120 mmol) was added to a solution of the sulfide (5 g, 30 mmol) in acetic acid (60 cm^3). The cloudy suspension was stirred at 50 °C for 3 h, cooled, poured into water (500 cm^3), and extracted with dichloromethane (4 × 100 cm^3). The combined extracts were washed repeatedly with aqueous sodium hydrogen carbonate and water until the acid had been neutralised and then dried ($MgSO_4$) and evaporated under reduced pressure. The residue was recrystallised from pentane to yield the sulfone[13] (quantitative) as needles; δ_H(250 MHz; $CDCl_3$) 7.56–7.50 (2 H, m), 6.9–6.8 (3 H, m) and 1.21 (9 H, s).

The sulfones **3a**, **b** and **c** were prepared by *ortho*-lithiation of *tert*-butyl phenyl sulfone using the method of Snieckus.[13]

tert-*Butyl* 2-[*Methoxy*(3-*methoxyphenyl*)*methyl*]*phenyl Sulfone* **3d**.—Butyllithium (1.6 mol dm^{-3} solution in hexane; 1.8 cm^3, 2.9 mmol) was added dropwise to a stirred solution of *tert*-butyl phenyl sulfone (500 mg, 2.5 mmol) in THF (35 cm^3) at −70 °C under nitrogen. After 30 min, *m*-anisaldehyde (0.34 cm^3, 2.8 mmol) was added dropwise to the yellow solution, and the reaction mixture warmed to room temp. over 2 h. Saturated aqueous ammonium chloride (100 cm^3) and water were added to the mixture which was then extracted with CH_2Cl_2 (3 × 30 cm^3). The combined extracts were washed with water, dried ($MgSO_4$) and evaporated to give a crude product, which was purified by flash chromatography (eluting with light petroleum–EtOAc, 1:1) to afford tert-*butyl* 2-[*hydroxy*(3-*methoxyphenyl*)*methyl*]*phenyl sulfone* (739.9 mg, 88%) as needles, m.p. 137–138 °C (Found: C, 64.7; H, 6.7; $C_{18}H_{22}O_4$ requires C, 64.64; H, 6.63%); R_F [light petroleum (b.p. 60–80 °C)–EtOAc, 1:1] 0.50; δ_H(250 MHz; $CDCl_3$), 7.97 (1 H, dd, *J* 7.8 and 1.5), 7.56 (1 H, dt, *J* 1.5 and 7.5), 7.45 (1 H, dt, *J* 1.6 and 7.5), 7.38 (1 H, dd, *J* 7.8 and 1.4), 7.27 (1 H, t, *J* 8.0), 7.11 (1 H, s), 7.01 (1 H, d, *J* 7.8), 6.83 (1 H, dd, *J* 8.2 and 2.5) (ArH × 8), 6.79 (1 H, d, *J* 4.2, C*H*OH), 3.82 (3 H, s, OMe), 3.33 (1 H, br d, *J* 4, CHO*H*) and 1.47 (9 H, s, CMe_3); δ_C(63 MHz; $CDCl_3$) 159.6, 146.1, 143.8, 134.2, 133.1, 133.0, 130.4, 129.3, 127.8, 118.7, 112.8, 112.0 (Ar × 12), 70.4 (CHOH), 61.3 (*C*Me_3), 55.2 (OMe) and 23.7 (C*Me*$_3$); *m*/*z* 352 (M + 18, 100%) and 317 (M − OH, 80).

Sodium hydride (80% suspension in mineral oil; 55 mg, 1.8 mmol) was added to a stirred solution of this alcohol (372 mg, 1.11 mmol) in THF (10 cm^3) at 0 °C under nitrogen. After 20 min, methyl iodide (0.2 cm^3) was added to the mixture which was then stirred at room temp. After this, the mixture was treated with saturated aqueous ammonium chloride (50 cm^3) and extracted with CH_2Cl_2 (3 × 20 cm^3). The combined extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure to give a crude product which was purified by filtration through silica to yield the *methyl ether* **3d** (384.2 mg, 99%) as a solid, m.p. 93–94 °C; R_F (light petroleum–EtOAc, 3:1) 0.30; δ_H(250 MHz; $CDCl_3$) 7.94 (1 H, dd, *J* 8.0 and 1.2), 7.80 (1 H, dd, *J* 8.0 and 1.1), 7.60 (1 H, dt, *J* 1.2 and 7.7), 7.41 (1 H, dd, *J* 1.2 and 7.8), 7.25 (1 H, t, *J* 8.0), 7.16 (2 H, m,), 6.77 (1 H, ddd, *J* 7.9, 2.3 and 1.1) (ArH × 8), 6.50 (1 H, s, C*H*OMe), 3.80 (3 H, s), 3.44 (3 H, s) (OMe × 2) and 1.41 (9 H, s, CMe_3); δ_C(63 MHz; $CDCl_3$) 159.7, 144.3, 142.7, 138.0, 132.7, 132.0, 130.0, 129.4, 127.3, 119.17, 112.9, 112.4 (Ar × 12), 78.7 (*C*HOMe), 61.0 (*C*Me_3), 57.3, 55.1 (OMe × 2) and 23.4 (C*Me*$_3$); *m*/*z* 348 (M^+, 6%), 317 (M − OMe, 46) and 259 (M − C_6H_4OMe, 100).

2-(tert-*Butylsulfonyl*)-N,N-*diisopropylbenzamide* **3e**.—Butyllithium (1.6 mol dm^{-3} solution in hexane; 26 cm^3, 41.6 mmol) was added dropwise to a stirred solution of the *N*,*N*-diisopropylbenzamide (8.2 g, 40 mmol) in THF (150 cm^3) at −70 °C under nitrogen. After 30 min, di-*tert*-butyl disulfide (9.6 cm^3, 50 mmol) was added dropwise to the yellow solution, which was then warmed to room temp. over 1 h, treated with water (500 cm^3) and extracted with CH_2Cl_2 (3 × 100 cm^3). The combined extracts were washed with water (2 × 100 cm^3), dried ($MgSO_4$) and evaporated to give a crude product, which was purified by flash chromatography (eluting with pentane–EtOAc, 12:1) to yield 2-(tert-*butylsulfonyl*)-N,N-*diisopropylbenzamide* (7.61 g, 68%) as a solid, m.p. 89–90 °C (Found: C, 69.65; H, 9.3; N, 4.7; $C_{17}H_{27}NOS$ requires C, 69.6; H, 9.27; N, 4.77%); R_F (light petroleum–EtOAc, 3:1) 0.50; δ_H(250 MHz; $CDCl_3$) 7.6–7.2 (4 H, m, ArH), 3.50 (1 H, septet, *J* 6.7, C*H*Me_2), 3.45 (1 H, septet, *J* 6.7, C*H*Me_2), 1.60 (3 H, d, *J* 6.6) and 1.57 (3 H, d, *J* 6.8) (CH*Me*$_2$), 1.49 (9 H, s, CMe_3), 1.21 (3 H, d, *J* 6.6) and 1.00 (3 H, d, *J* 6.4) (CH*Me*$_2$); δ_C(63 MHz; $CDCl_3$) 169.1 (C=O), 145.2, 138.1, 129.2, 128.9, 127.7, 126.0 (Ar), 50.7 (*C*HMe_2), 47.5 (*C*Me_3), 45.6 (*C*HMe_2), 31.6 (C*Me*$_3$), 20.8, 20.7, 20.3 and 19.9 (CH*Me*$_2$ × 2); *m*/*z* 294 (M + 1, 100%).

This sulfide (6.09 g, 20.7 mmol) was oxidised with sodium perborate by the method described above, to yield, without further purification, the *sulfone* **3e** (6.48 g, 96%) as a waxy solid, m.p. 128–132 °C (Found: C, 63.4; H, 8.3; N, 4.3; $C_{17}H_{27}NO_3S$ requires C, 62.7; H, 8.36; N, 4.30%); R_F (pentane–EtOAc, 1:1) 0.44; δ_H(250 MHz; $CDCl_3$) 7.87 (1 H, dd, *J* 7.9 and 1.0, ArH), 7.64 (1 H, dt, *J* 1.2 and 7.4, ArH), 7.50 (1 H, dt, *J* 1.3 and 7.5, ArH), 7.28 (1 H, dd, *J* 7.4 and 1.2, ArH), 3.48 (1 H, septet, *J* 6.9, C*H*Me_2), 3.38 (1 H, septet, *J* 6.9, C*H*Me_2), 1.55 (3 H, d, *J* 6.9), 1.53 (3 H, d, *J* 6.9) (CH*Me*$_2$), 1.38 (9 H, s, CMe_3) and 1.24 (3 H, d, *J* 6.6) and 0.99 (3 H, d, *J* 6.6) (CH*Me*$_2$); δ_C(63 MHz; $CDCl_3$) 167.6 (C=O), 140.2, 135.6, 132.4, 132.2, 127.9, 127.5 (Ar), 61.3 (Me_3C), 51.0, 45.7 (*C*HMe_2 × 2), 24.1 (C*Me*$_3$), 20.4, 20.3, 19.4 and 19.1 (CH*Me*$_2$ × 2); *m*/*z* 326 (M + 1, 4%), 310 (M − Me, 48) and 152 (100).

tert-*Butyl* 2-*Methoxyphenyl Sulfone* **3f**.—Anisole was lithiated by the method of Finnegan and Altschuld.[41] Butyllithium (1.6 mol dm^{-3} solution in hexane; 31 cm^3) was added by dropping funnel to a solution of anisole (5.5 cm^3, 51 mmol) in THF at 0 °C under nitrogen. The solution was stirred for 23 h at room temp., and then cooled to 0 °C and treated with a solution of di-*tert*-butyl disulfide (10 cm^3, 52 mmol) in THF (20 cm^3). Stirring was continued at 0 °C for 20 min after which the solution was warmed to room temp., treated with saturated aqueous ammonium chloride and extracted with CH_2Cl_2. The combined extracts were washed with 5% aqueous sodium hydroxide and water, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash chromatography (eluting with pentane–diethyl ether, 49:1 then 19:1) to give tert-*butyl* 2-*methoxyphenyl sulfide* (2.02 g, 20%) as a liquid (Found: C, 67.3; H, 8.1; $C_{11}H_{16}OS$ requires C, 67.3; H, 8.21%); R_F (pentane–Et_2O, 19:1) 0.33; δ_H(250 MHz; $CDCl_3$) 7.52 (1 H, dd, *J* 7.9 and 1.6, ArH), 7.36 (1 H, dt, *J* 1.8 and 8.0, ArH), 6.92 (2 H, m, ArH), 3.86 (3 H, s, OMe) and 1.30 (9 H, s, CMe_3); δ_C(63 MHz; $CDCl_3$) 161.2, 140.3, 130.7, 120.6, 120.4, 111.0 (Ar), 55.5 (OMe), 46.8 (*C*Me_3) and 30.9 (C*Me*$_3$); *m*/*z* 197 (M + 1, 100%).

This sulfide (1.65 g, 8.4 mmol) was oxidised with sodium perborate by the method described above to give the *sulfone* **3f** (1.806 g, 94%) as an off-white solid, m.p. 74–74.5 °C (Found: C, 57.9; H, 7.1; $C_{11}H_{16}OS$ requires C, 57.9; H, 8.06%); R_F (light petroleum–EtOAc, 3:1) 0.10; δ_H(250 MHz; $CDCl_3$) 7.91 (1 H, dd, *J* 7.9 and 1.6, ArH), 7.60 (1 H, dt, *J* 1.4 and 8.1, ArH), 7.09 (1 H, t, *J* 7.7, ArH), 7.05 (1 H, d, *J* 8.2, ArH), 3.92 (3 H, s, OMe) and 1.37 (9 H, s, CMe_3); δ_C(63 MHz; $CDCl_3$) 159.0, 135.5, 134.2, 123.5, 120.3, 112.8 (Ar), 61.2 (Me_3C), 57.0 (OMe) and 23.8 (C*Me*$_3$); *m*/*z* 246 (M + 18, 100%) and 229 (M + 1, 56).

2-(tert-*Butylsulfonyl*)-N,N-*diisopropyl*-5-*methylbenzamide* **3g**.—Butyllithium (1.6 mol dm^{-3} solution in hexane; 1.0 cm^3, 1.6 mmol) was added dropwise to a stirred solution of the sulfone **3e** (491 mg, 1.5 mmol) in THF (10 cm^3) at −70 °C under nitrogen. After 30 min, methyl iodide (0.2 cm^3) was added dropwise to the yellow solution, and the reaction mixture was warmed to room temp. over 2 h. Saturated aqueous ammonium chloride (100 cm^3) and water were added to the mixture which was then extracted with CH_2Cl_2 (3 × 30 cm^3). The combined extracts were washed with water, dried ($MgSO_4$) and evaporated to give a crude product, which was purified by flash chromatography (eluting with light petroleum–EtOAc, 3:1) to give the *sulfone* **3g** (331.5 mg, 66%) as an oil (Found: C, 64.6; H, 8.9; N, 4.0; $C_{18}H_{29}NO_3S$ requires C, 63.68; H, 8.61; N, 4.13%); R_F

(pentane–EtOAc, 1:1) 0.58; δ_H(250 MHz; $CDCl_3$) 7.48 (1 H, t, *J* 7.6, ArH), 7.31 (1 H, d, *J* 7.6, ArH), 7.11 (1 H, d, *J* 7.3, ArH), 3.47 (1 H, septet, *J* 6.8, C*H*Me_2), 3.38 (1 H, septet, *J* 6.9, C*H*Me_2), 2.80 (3 H, s, Ar*Me*), 1.56 (3 H, d, *J* 6.8), 1.53 (3 H, d, *J* 6.9 (CH*Me*$_2$), 1.43 (9 H, s, CMe_3), 1.22 (3 H, d, *J* 6.6) and 0.98 (3 H, d, *J* 6.6) (CH*Me*$_2$); δ_C(63 MHz; $CDCl_3$) 168.9 (C=O), 142.3, 141.2, 133.0, 132.9, 131.6, 126.1 (Ar), 63.6 (Me_3C), 58.8, 45.7 (*C*HMe_2 × 2), 24.9 (*CMe*$_3$), 22.8 (Ar*Me*), 20.3, 20.2, 19.4 and 19.1 (CH*Me*$_2$ × 2); *m*/*z* 340 (M + 1, 100%).

tert-*Butyl* 2-*Methoxy*-5-*methylphenyl Sulfone* **3h**.—By the same method, the sulfone **3f** (450.6 mg, 2.0 mmol) was methylated and the crude product was purified by flash chromatography (eluting with light petroleum–EtOAc, 1:1) to yield the *sulfone* **3h** (454 mg, 95%) as an oil; R_F (light petroleum–EtOAc, 1:1) 0.34; δ_H(250 MHz; $CDCl_3$) 7.40 (1 H, t, *J* 8.0, ArH), 6.91 (2 H, m, ArH), 3.87 (3 H, s, OMe), 2.71 (3 H, s, ArMe) and 1.39 (9 H, s, CMe_3); δ_C(63 MHz; $CDCl_3$) 160.5, 143.7, 134.0, 125.7, 112.7, 111.6 (Ar), 62.8 (Me_3C), 56.4 (OMe), 23.7 (*CMe*$_3$) and 23.4 (Ar*Me*); *m*/*z* 260 (M + 18, 95%) and 243 (M + 1, 100).

tert-*Butyl* 4-*Methoxyphenyl Sulfone* **3i**.—By the method described above for the synthesis of *tert*-butyl phenyl sulfone, 4-hydroxybenzenethiol gave *tert*-butyl 4-hydroxyphenyl sulfide (90%).

This phenol was methylated by the method of Vyas and Shah.[42] Sodium hydroxide (8 g) in water (40 cm^3) and dimethyl sulfate (20 g) were added alternately in five portions to a solution of the phenol in ethanol (50 cm^3). The mixture was refluxed for 3 h, after which most of the ethanol was distilled off. 10% Aqueous ammonia (100 cm^3) was added to the solution which was then extracted with ether (3 × 40 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure to yield a residue which was distilled to give *tert*-butyl 4-methoxyphenyl sulfide[43] (9.2 g, 61%), b.p. 108 °C (8 mmHg); δ_H(250 MHz; $CDCl_3$) 7.45 (2 H, d, *J* 8.8), 6.88 (2 H, d, *J* 8.8), 3.82 (3 H, s) and 1.30 (9 H, s); δ_C(63 MHz; $CDCl_3$) 161, 139, 125, 115, 55, 46 and 33.

The sulfide was oxidised with sodium perborate by the method described above to give the sulfone[44] **3i** (quantitative); δ_H(250 MHz; $CDCl_3$) 7.80 (2 H, d, *J* 8.8), 7.02 (2 H, d, *J* 8.8), 3.90 (3 H, s) and 1.39 (9 H, s).

General Procedure for the Substitution and Reduction of Aryl tert-*Butyl Sulfones*.—The following procedure was used in all cases, subject to modifications mentioned in the tables of results. The Grignard reagent (methylmagnesium bromide: 22% in THF; butylmagnesium bromide: 2 mol dm^{-3} in THF; isopropylmagnesium chloride: 1 mol dm^{-3} in THF; phenylmagnesium bromide: 3 mol dm^{-3} in diethyl ether; *p*-tolylmagnesium bromide: 1 mol dm^{-3} in diethyl ether; *o*-tolylmagnesium bromide: 1 mol dm^{-3} in THF, all used as commercially supplied) was added dropwise to a stirred solution of the sulfone (between 0.25 and 1 mmol) and the catalyst (3.5–5 mol%, dried by heating under vacuum and introduced as a solution in THF) in dry THF (10 cm^3 $mmol^{-1}$) at 0 °C under nitrogen. The cooling bath was removed. At the end of the reaction time, the reaction was quenched with water and an internal GC standard (decane, 1 equiv.) was added. The mixture was extracted with CH_2Cl_2. The combined organic fractions were washed with water, dried ($MgSO_4$) and analysed by GC and GC–MS. Yields were corrected by comparing the response of the standard with that of authentic samples of the products or compounds similar in structure to the products. Assignments were made by comparison with known compounds or by the masses observed by GC–MS.

In those cases where the products were isolated, the solvent was evaporated under reduced pressure and the crude products were purified by flash chromatography.

N,N-*Diisopropyl*-2-*phenylbenzamide* **4a**.—Following the general procedure and using the conditions given in Table 2, entry 8, the sulfone **3e** (319.2 mg, 1.0 mmol) gave, after flash chromatography (eluting with light petroleum–EtOAc, 6:1) the amide[45] **4a** (222.3 mg, 81%) as an oil; R_F (light petroleum–EtOAc, 6:1) 0.20; δ_H(250 MHz; $CDCl_3$) 7.6–7.15 (8 H, m, ArH), 3.57 (1 H, br m, C*H*Me_2), 3.22 (1 H, br septet, *J* 6.4, C*H*Me_2), 2.25 (3 H, s, ArMe), 1.49 (3 H, d, *J* 6.5), 1.07 (3 H, d, *J* 6.5), 1.00 (3 H, br s) and 0.55 (3 H, br s) (CH*Me*$_2$ × 2); δ_C(63 MHz; $CDCl_3$) 169.8 (C=O), 140–120 (broad humps), 50.2, 45.3 (NCH × 2), 20.9, 20.7, 20.3 and 19.6 (Me × 4). The signals in the NMR spectra of this compound are broadened considerably by slow interconversion of rotamers.

N,N-*Diisopropyl*-2-(4-*methylphenyl*)*benzamide* **4b**.—Following the general procedure and using the conditions given in Table 2, entry 10, sulfone **3e** (322.8 mg, 1.0 mmol) gave, after flash chromatography (eluting with light petroleum–EtOAc, 6:1) the amide[46] **4b** (252 mg, 86%) as an oil; R_F (light petroleum–EtOAc, 6:1) 0.21; δ_H(250 MHz; $CDCl_3$) 7.50–7.15 (8 H, m, ArH), 2.53 (1 H, sept, *J* 6.8, C*H*Me_2), 3.25 (1 H, sept, *J* 6.8, C*H*Me_2), 2.38 (3 H, s, Ar*Me*), 1.53 (3 H, d, *J* 6.9), 1.32 (3 H, d, *J* 6.9), 0.90 (3 H, d, *J* 6.6) and 0.36 (3 H, d, *J* 6.6) (CH*Me*$_2$ × 2); δ_C(63 MHz; $CDCl_3$) 170.4, 137.8, 137.2, 136.9, 129.1, 128.9, 128.4, 127.3, 126.5 (Ar), 50.5, 45.5 (NCH × 2), 21.1, 20.8, 20.7, 19.5 and 19.4 (Me × 5).

N,N-*Diisopropyl*-2-(2-*methylphenyl*)*benzamide* **4c**.—Following the general procedure and using the conditions given in Table 2, entry 12, the sulfone **3e** (325.5 mg, 1.0 mmol) gave, after flash chromatography (eluting with light petroleum–EtOAc, 5:1) the amide[47] **4c** (123 mg, 42%) as an oil; R_F (light petroleum–EtOAc, 3:1) 0.37. The signals in the ^1H and ^{13}C NMR spectra of this compound were broadened by slow interconversion of rotamers.

2-*Methoxy*-4′-*methylbiphenyl* **4d**.—Following the general procedure and using the conditions given in Table 2, entry 16, the sulfone **3f** (196 mg, 1.0 mmol) gave, after flash chromatography (eluting with pentane) the ether[48] **4d** (109 mg, 55%) as an oil; δ_H(250 MHz; $CDCl_3$) 7.50 (2 H, d), 7.45–7.3 (4 H, m), 7.2–7.0 (2 H, m), 3.83 (3 H, s) and 2.40 (3 H, s); δ_C(63 MHz; $CDCl_3$) 156, 137, 136, 132, 129, 128, 121, 110, 55 and 22.

N,N-*Diisopropyl*-3-*methyl*-2-(4-*methyl*)*phenylbenzamide* **4e**.—Following the general procedure and by using the conditions given in Table 2, entry 17, the sulfone **3g** (65.8 mg, 0.19 mmol) gave, after flash chromatography (eluting with light petroleum–EtOAc, 5:1) the *amide* **4e** (27.4 mg, 47%) as an oil; R_F (light petroleum–EtOAc, 3:1) 0.38; δ_H(250 MHz; $CDCl_3$) 7.4–7.0 (7 H, br m, ArH), 3.61 (1 H, br sept, *J* 6.6, C*H*Me_2), 3.19 (1 H, br sept, *J* 6.6, C*H*Me_2), 2.38 (3 H, br s, Ar*Me*), 2.18 (3 H, br s, Ar*Me*), 1.45 (3 H, br d, *J* 6.5), 1.02 (3 H, br d, *J* 6.7), 0.97 (3 H, br d, *J* 6.5) and 0.66 (3 H, br d, *J* 6.5) (CH*Me*$_2$ × 2); δ_C(63 MHz; $CDCl_3$) 170.1 (C=O), 139.1, 136.6, 136.4, 135.2, 129.9, 127.1, 122.9 (Ar), 50.3, 45.2 (*C*HMe_2 × 2), 21.2, 20.9, 20.7, 20.6, 20.0 and 19.6 (Me × 6); *m*/*z* 310 (M + 1, 100%).

Starting material **3g** (26 mg, 40%) was also recovered from the column.

4-*Methoxy*-4′-*methylbiphenyl* **4f**.—Following the general procedure and by using the conditions given in Table 2, entry 19, the sulfone **3f** (196 mg, 1.0 mmol) gave, after flash chromatography (eluting with pentane) the ether[49] **4d** (117 mg, 59%) as needles.

2-Methylsulfonylphenyl Octyl Sulfone **7**.—1,2-Dichlorobenzene (3.0 cm^3, 26.5 mmol) was added to a stirred solution of sodium octanethiolate (4.27 g, 25.4 mmol; made by the method of Tiecco)[40] in hexamethylphosphoramide (HMPA; 120 cm^3), and the mixture was heated to 80 °C for 21 h. It was then cooled to room temp., treated with saturated brine (400 cm^{-3}) and extracted with ether (3 × 100 cm^{-3}). The combined extracts were washed with water, dried ($MgSO_4$) and evaporated. The crude product was purified by flash chromatography (eluting with pentane) to give *2-chlorophenyl octyl sulfide* (5.0 g, 79%) as a liquid (Found: C, 65.6; H, 8.1; $C_{14}H_{19}ClS$ requires C, 65.46; H, 8.24%); R_F (pentane) 0.31; δ_H(250 MHz; $CDCl_3$) 7.37 (1 H, d, *J* 7.9, ArH), 7.25 (2 H, m, ArH × 2), 7.09 (1 H, dt, *J* 2.0 and 7.6, ArH), 2.94 (2 H, t, *J* 7.3, CH_2S), 1.71 (2 H, quint., *J* 7.4, CH_2CH_2S), 1.48 (2 H, m, $CH_2CH_2CH_2S$), 1.45–1.25 (8 H, m, $[CH_2]_4Me$) and 0.90 (3 H, t, *J* 7.0, Me); δ_C(63 MHz; $CDCl_3$) 136.6, 132.9, 129.5, 127.6, 127.0, 125.9 (Ar), 32.3, 31.8, 29.2, 29.0, 28.6, 22.7 and 14.1; *m/z* 257 (M + 1, 75%) and 256 (M^+, 100).

Sodium methanethiolate (0.830 g, 11.8 mmol) was added to a stirred solution of this sulfide (2.57 g, 10 mmol) in HMPA (50 cm^3), and the mixture heated to 60 °C for 18 h. More sodium methanethiolate (0.358 g, 5.1 mmol) was added to the mixture which was then heated to 80 °C for 30 min. Work-up as described above gave a crude oil, most of which was oxidised without purification. A small amount was purified by flash chromatography (eluting with pentane–Et_2O, 99:1) to give *2-methylsulfanylphenyl octyl sulfide* as a liquid; R_F (pentane–Et_2O, 49:1) 0.30; δ_H(250 MHz; $CDCl_3$) 7.32 (1 H, d, *J* 7.1, ArH), 7.2–7.1 (3 H, m, ArH × 3), 2.92 (2 H, t, *J* 7.3, CH_2S), 2.46 (3 H, s, MeS), 1.68 (2 H, quint., *J* 7.3, CH_2CH_2S), 1.44 (2 H, m, $CH_2CH_2CH_2S$), 1.4–1.2 (8 H, m, $[CH_2]_4Me$) and 0.90 (3 H, t, *J* 7.0, $MeCH_2$); δ_C(63 MHz; $CDCl_3$) 139.7, 135.0, 129.8, 126.7, 125.6, 125.1, 33.7, 31.6, 29.2, 29.2, 20.0, 28.9, 22.6, 15.9 and 14.1; *m/z* 286 (M + 18, 100%).

Sodium perborate (7.80 g, 50.7 mmol) was added to a stirred solution of the crude bis(sulfide) (10 mmol) in glacial acetic acid. The mixture was heated to 60 °C for 90 min and then allowed to cool to room temp. over a further 66 h. The suspension was then poured into water and extracted with CH_2Cl_2 (3 × 100 cm^3). The combined extracts were washed with water, saturated aqueous sodium hydrogen carbonate, and water, dried ($MgSO_4$) and evaporated under reduced pressure to yield a crude oil. This was purified by flash chromatography (eluting with light petroleum–ether, 2:1) to give the *bis(sulfone)* **7** (738 mg, 22% from **3**) as an oil (Found: C, 54.5; H, 7.3%. $C_{15}H_{24}S_2O_4$ requires C, 54.19; H, 7.28%); R_F (EtOAc–light petroleum, 1:1) 0.43; δ_H(250 MHz; $CDCl_3$) 8.36 (1 H, m, ArH), 8.28 (1 H, m, ArH), 7.86 (2 H, AA'BB' m, ArH × 2), 3.61 (2 H, m, SO_2CH_2), 3.43 (3 H, s, $MeSO_2$), 1.69 (2 H, m, SCH_2CH_2), 1.4–1.1 (10 H, m, $[CH_2]_5$) and 0.83 (3 H, t, *J* 6.5, CH_2Me); δ_C(63 MHz; $CDCl_3$) 140.2, 138.9, 134.2, 134.1, 133.3, 132.5 (Ar), 56.7 (SO_2CH_2), 45.4 (SO_2Me), 31.6, 28.9, 28.8, 28.1, 22.5, 22.3 and 14.0; *m/z* 350 (M + 18, 100%) and 333 (M + 1, 8).

2-Butylphenyl Methyl Sulfone **9**.—Butyllithium (1.6 mol dm^{-3} solution in hexane; 0.38 cm^3, 0.6 mmol) was added dropwise to a stirred solution of the sulfone **11** (47 mg, 0.2 mmol) in dry THF (4 cm^3) at 0 °C under nitrogen. The mixture was stirred at room temp. for 20 h and then quenched with water and extracted with CH_2Cl_2. The combined extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure, to give a crude product which was analysed by GC and GC–MS. Flash chromatography of the crude product (eluting with pentane–EtOAc, 4:1, and then 2:1) gave the title sulfone[50] **9** (30.2 mg, 75%) as an oil, R_F (EtOAc–pentane, 1:1) 0.65; δ_H(250 MHz; $CDCl_3$) 8.05 (1 H, dd, *J* 7.0 and 1.0, ArH), 7.58 (1 H, dt, *J* 1.0 and 6.8, ArH), 7.40 (1 H, dd, *J* 6.8 and 1.0, ArH), 7.39 (1 H, dt, *J* 1.0 and 6.8, ArH), 3.10 (3 H, s, $MeSO_2$), 3.06 (2 H, m, $ArCH_2$), 1.70 (2 H, m, $ArCH_2CH_2$), 1.48 (2 H, sextet, *J* 6.8, CH_2Me) and 0.98 (3 H, t, *J* 6.9, CH_2Me); δ_C(63 MHz; $CDCl_3$) 142.8, 135.5, 131.6, 129.4, 126.5 (ArH), 44.7 ($MeSO_2$), 34.1, 32.7, 22.6 and 13.7 (Bu); *m/z* 230 (M + 18, 100%).

GC–MS Analysis of the crude product mixture indicated the presence of 10% starting material and 10% methyl phenyl sulfone.

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