Pergamon

Tetrahedron Vol. 51, No. 9, pp. 2699-2708, 1995

0040-4020/95 $9.50+0.00

0040-4020(94)01116-8

Arene-catalysed Reductive Desulfonylation and Desulfinylation Reactions: New Routes for Alkyllithiums

Emma Alonso, David Guijarro and Miguel Yus*

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain

Abstract: The reaction of alkyl phenyl sulfones (**1**) with an excess of lithium powder and a catalytic amount of naphthalene (8 mol %) in the presence of a carbonyl compound or chlorotrimethylsilane (Barbier-type conditions) in THF at temperatures ranging between -78 and 20°C leads, after hydrolysis, to the expected products (**2**) arising from the corresponding alkyllithium generated *in situ*. When the same methodology is applied to sulfolene (**3**) or different alkyl phenyl sulfoxides (**6**), cyclic sulfinates **5** or products **2** are, respectively, obtained, the yields being, in general modest.

INTRODUCTION

Sulfones and sulfoxides are doubtless the most important sulfur-containing organic compounds in synthetic organic chemistry[1]. In the case of sulfones[2], they have been widely used in carbon-carbon formation reactions through the corresponding α-carbanions. However, since the sulfone functionality is rarely present in the target molecule, it has to be removed at the end of the synthesis, mainly by a reductive desulfonylation process[3] (specially useful in the case of alkyl aryl sulfones). For this purpose the use of electropositive metals in the presence of a proton source has been shown to be very effective[4,5], so the corresponding sulfone/hydrogen exchange can be easily carried out following this methodology. Although in all these reductive desulfonylation reactions a carbanionic intermediate is assumed to be formed, it has been never trapped with other electrophile different than a proton[6,7]. In the case of sulfoxides, the normal desulfinylation reaction, at the end of the synthesis, is by a β-elimination[1], the corresponding reductive desulfinylation for simple sulfoxides being unknown, to our best knowledge[8]. In this paper we describe for the first time a reductive desulfonylation and desulfinylation reaction of sulfones and sulfoxides, respectively, using an arene-catalysed lithiation[9,10], which represents both a new type of reactivity of sulfones and sulfoxides, as well as a new route for organolithium reagents[11].

RESULTS AND DISCUSSION

The reaction of different alkyl phenyl sulfones **1** (prepared by nucleophilic substitution from the corresponding alkyl bromides with sodium benzenesulfinate[12]) with an excess of lithium powder (1:14 molar ratio) and a catalytic amount of naphthalene (1:0.16 molar ratio; 8 mol %)[13] in the presence of a carbonyl compound (isobutyraldehyde, benzaldehyde, 2-pentanone or cyclohexanone) or chlorotrimethylsilane (1:1.2 molar ratio; Barbier-type reaction conditions) in THF at temperatures ranging between -78 and 20°C gave, after hydrolysis with water, the expected coupling products **2aa-2de** in moderate yields (Scheme 1 and Table 1). Although the reaction can be applied to primary, secondary, allylic and benzylic intermediates, the secondary sulfone **1c** gave the best results working at -30 to 20°C (Table 1, entries 5 and 6, and footnote i). In some cases we found that the yield was higher when the process was carried out in the presence of boron trifluoride etherate: in absence of this co-reagent compounds **2aa**, **2ab**, **2ba**, **2db** and **2dd** were obtained in 46, 17, 23, 20 and 50% yield, respectively, these values being lower than the corresponding ones using this additive (compare to Table 1, entries 1-3, 8 and 10, respectively).

$$\mathrm{PhSO_2R} \xrightarrow{\text{i,ii}} \mathrm{RE}$$

2

1a : R=Et
1b : $R=CH_2=CHCH_2$
1c : $R=Pr^i$
1d : $R=PhCH_2$

Scheme 1. *Reagents and conditions*: i, Li powder, $C_{10}H_8$ cat. (8 mol %), $E^+=Pr^iCHO$, PhCHO, Et_2CO, $(CH_2)_5CO$, Me_3SiCl, THF, -78 to 20°C; ii, H_2O.

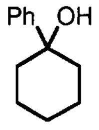
In all the reactions shown in Scheme 1, using a carbonyl compound as electrophile, we found a small amount (<10%, GLC) of the corresponding pinacol-type compound as by-product. In other cases, when the yield was lower we found other by-products. Thus, in the preparation of compound **2ab** we could isolate a 11% of 1-phenylcyclohexanol (**2'ab**) resulting from the formation of phenyllithium as a minor intermediate in the reductive desulfonylation of the starting material **1a** (Table 1, entry 2 and footnote e). On the other hand, in the preparation of products **2bb** and **2cb** we isolated the cyclohexanol derivatives **2'bb** and **2'cb**, respectively, in 11 and 14% yields, respectively. In the case of compound **2'bb** the deprotonation of the starting allyl sulfone gives the intermediate **II**, which by α-addition to cyclohexanone leads to the alcoholate **III**; the last *in situ* tandem desulfonylation-abstraction of a proton affords the more stable final product **2'bb** through the dianion **IV**. The formation of compound **2'cb** can be rationalised by addition of α-lithioisopropyl phenyl sulfone to the electrophile (→**I**) followed by β-elimination of phenyl sulfinic acid.

The reaction shown in Scheme I is not applicable to vinylic sulfones. Thus, when sulfones **1e,f**[14] were treated under the same reaction conditions as for compound **1a**, using benzaldehyde as the electrophile, diphenylcarbinol was the only coupling product isolated (25 and 49%[15] yield, respectively). This result indicates clearly that in the case of vinyl sulfones the sulfone-phenyl bond reductive cleavage is preferred instead of the corresponding sulfone-vinyl one.

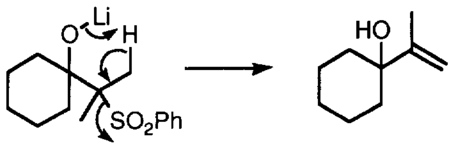
Table 1. Preparation of Compounds **2** from Phenyl Sulfones **1**

Entry	Starting sulfone **1**	Electrophile E^+	Product **2**[a]				
			No.	R	E	Yield(%)[b]	R_f[c]
1[d]	**1a**	PhCHO	**2aa**	Et	PhCHOH	61	0.35
2[d]	**1a**	$(CH_2)_5CO$	**2ab**	Et	$(CH_2)_5COH$	32[e]	0.30[f]
3[d]	**1b**	PhCHO	**2ba**	$CH_2{=}CHCH_2$	PhCHOH	47	0.54[g]
4	**1b**	$(CH_2)_5CO$	**2bb**	$CH_2{=}CHCH_2$	$(CH_2)_5COH$	22[h]	0.46[g]
5[i]	**1c**	PhCHO	**2ca**	Pr^i	PhCHOH	30	0.76
6[i]	**1c**	$(CH_2)_5CO$	**2cb**	Pr^i	$(CH_2)_5COH$	17[j]	0.53
7	**1d**	Pr^iCHO	**2da**	$PhCH_2$	Pr^iCHOH	46	0.54
8[d]	**1d**	PhCHO	**2db**	$PhCH_2$	PhCHOH	34	0.54
9	**1d**	Et_2CO	**2dc**	$PhCH_2$	Et_2COH	54	0.44
10[d]	**1d**	$(CH_2)_5CO$	**2dd**	$PhCH_2$	$(CH_2)_5COH$	57	0.30
11	**1d**	Me_3SiCl	**2de**	$PhCH_2$	Me_3Si	44	0.43[k]

[a] All products **2** were >95% pure (GLC and 300 MHz ^1H NMR). [b] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on the starting sulfone **1**. [c] Silica gel, hexane/ethyl acetate: 6/1. [d] The reaction was carried out in the presence of $BF_3{\cdot}OEt_2$ (1:2.2 molar ratio). [e] A 11% of 1-phenylcyclohexanol (**2'ab**) was also obtained. [f] Silica gel, hexane/ethyl acetate: 9/1. [g] Silica gel, hexane/ethyl acetate: 4/1. [h] A 11% of (*E*)-1-(1-propenyl)cyclohexanol (**2'bb**) was also obtained. [i] The reaction was performed at temperatures ranging between -30 and 20°C. [j] A 14% of 1-(1-methylvinyl)cyclohexanol (**2'cb**) was also obtained. [k] Silica gel, hexane.

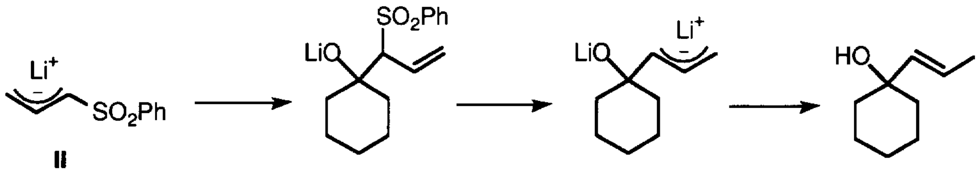


2'ab

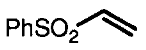


I

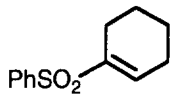
2'cb



II **III** **IV** **2'bb**



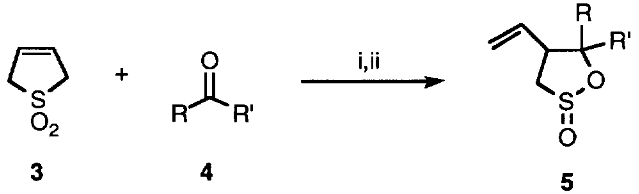
1e



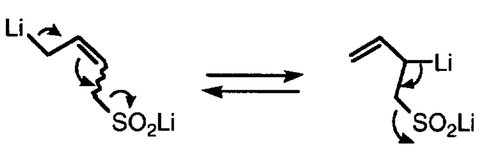
1f

It is noteworthy that the *in situ* formed organolithium intermediate involved in Scheme 1 survives under the reaction conditions and prefers to react with the electrophile present in the reaction medium instead of abstracting a proton from the α-position of the starting sulfone **1**. This is a consequence of working under Barbier-type reaction conditions at low temperature: when the reaction was performed in two steps, first lithiation and then (after disappearing of the starting sulfone) the reaction with the electrophile, no reaction products of the type **2** were isolated, although the starting material was completely consumed.

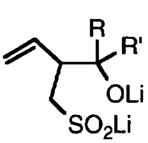
In order to study the possibility of obtaining dianionic species we considered the reductive desulfonylation of commercially available sulfolene **3**. When the same reaction described in Scheme 1 was applied to this starting material the unexpected cyclic sulfinates **5** were the only reaction products isolated in modest yields (Scheme 2 and Table 2). As a consequence of the existence of two or three stereocenters in the molecule, compounds **5** were isolated as a mixture of diastereoisomers, which almost in all cases was separated by column chromatography (see Experimental Part).



Scheme 2. *Reagents and conditions*: i, Li powder, $C_{10}H_8$ cat. (8 mol %), THF, -78 to 20°C; ii, H_2O.



V **VI**



VII

The isolation of compounds **5** can be explained considering the equilibrium between intermediates **V** and **VI** fomed by the initial sulfur-carbon reductive cleavage of sulfolene **3**. The reaction of intermediate **VI** with the carbonyl compound used as electrophile yields the dianion **VII**, which under the work-up acidic conditions cyclises to the obtained reaction products **5**. The low yields obtained in the reaction shown in Scheme 2 can be explained taking into account a possible δ- or β-elimination from **V** and/or **VI**, which leads to the formation of 1,3-butadiene; for this reason it is neccessary to work under Barbier-type reaction conditions.

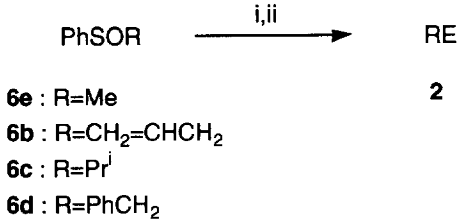
Table 2. Preparation of Compounds **5**

Entry	Carbonyl compound **4**		Product **5**[a]			
	R	R'	No.	Yield[b]	Isomers ratio[c]	R_f[d]
1	Pr^i	H	**5a**	14	3:2:1	0.66, 0.62[e]
2	Me	Me	**5b**	20	8:1	0.27[f]
3	Et	Et	**5c**	35	5:1	0.40, 0.29[g]
4	$-(CH_2)_4-$		**5d**	24	4:1	0.35[f]
5	$-(CH_2)_5-$		**5e**	25	4:1	0.38, 0.35[g]

[a] All products **5** were >95% pure (GLC and 300 MHz ^{1}H NMR). [b] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on the starting sulfolene **3**. [c] Deduced by GLC from the reaction crude. [d] Silica gel, hexane/ethyl acetate: 4/1. [e] Corresponding to the two major diastereoisomers. [f] R_f value corresponding to the major diastereoisomer. [g] Corresponding to both the major and the minor diastereoisomers, respectively.

In the last part of this paper we studied the reductive desulfinylation of alkyl phenyl sulfoxides. Thus, applying the same methodology shown in Scheme 1 to the corresponding sulfoxides, compounds **2** (resulting from the reaction of the *in situ* formed organolithium compounds RLi with the electrophile present in the reaction medium) were obtained (Scheme 3 and Table 3). We found in this case that the best results were obtained either using 4,4'-di-*tert*-butylbiphenyl (DTBB; 5 mol %) at 0 to 20°C (starting materials **6c** and **6e**) or naphthalene (8 mol %) at -78 to 20°C (starting materials **6b** and **6d**) as the arene catalysts. At other different temperatures and changing the arene component the corresponding yields were poorer. In some cases, when the yields are low, we found the corresponding alcohol (resulting from the reduction of the carbonyl compound used as electrophile) as the main product (Table 3, entries 2 and 5, and footnote e and g). Finally, it is noteworthy that the reaction does not need the presence of a phenyl group in the starting sulfoxide: when the reductive desulfinylation shown in Scheme 3 was applied to dimethyl sulfoxide and benzaldehyde, the corresponding reaction product was isolated in only 10% yield[14]. So the presence of the phenyl group in the starting sulfoxide facilitates the process and at the same time avoids the obtention of a mixture of products for unsymmetrical sulfoxides.

In conclusion, we have described here two new reactions, reductive desulfonylation and desulfinylation, which amplies the reactivity of sulfones and sulfoxides, respectively, allowing their transformation into alkyllithium reagents and the *in situ* reaction of these carbanionic intermediates with electrophilic reagents, mainly carbonyl compounds.



Scheme 3. *Reagents and conditions*: i, Li powder, $C_{10}H_8$ or DTBB (5-8 mol %), E^+=Pr^{i}CHO, PhCHO, Et_2CO, Ph_2CO, THF, -78 or 0 to 20°C (see Table 3); ii, H_2O.

Table 3. Preparation of Compounds **2** from Phenyl Sulfoxides **6**

Entry	Starting sulfoxide **6**	Electrophile E^+	Reaction conditions Arene	T (°C)	Product 2[a] No.	R	E	Yield (%)[b]	R_f[c]
1	**6e**	PhCHO	DTBB	0	**2ea**	Me	PhCHOH	40	0.34[d]
2	**6e**	Ph_2CO	DTBB	0	**2eb**	Me	Ph_2COH	14[e]	0.34
3	**6b**	PhCHO	$C_{10}H_8$	-78	**2ba**	CH_2=$CHCH_2$	PhCHOH	50	0.54[d]
4	**6b**	Et_2CO	$C_{10}H_8$	-78	**2bc**	CH_2=$CHCH_2$	Et_2COH	43	0.57[f]
5	**6c**	PhCHO	DTBB	0	**2ca**	Pr^i	PhCHOH	15[g]	0.76
6	**6d**	Pr^{i}CHO	$C_{10}H_8$	-78	**2da**	$PhCH_2$	Pr^{i}CHOH	35	0.54
7	**6d**	PhCHO	$C_{10}H_8$	-78	**2db**	$PhCH_2$	PhCHOH	51	0.54
8	**6d**	Et_2CO	$C_{10}H_8$	-78	**2dc**	$PhCH_2$	Et_2COH	58	0.44

[a] All products **2** were >93% pure (GLC and 300 MHz ^{1}H NMR). [b] Isolated yield after column chromatography (silica gel, hexane/ethyl acetate) based on the starting sulfoxide **6**. [c] Silica gel, hexane/ethyl acetate: 6/1. [d] Silica gel, hexane/ethyl acetate: 4/1. [e] A 36% (GLC) yield of diphenyl carbinol was also obtained. [f] Silica gel, hexane/ethyl acetate: 3/1. [g] A 25% (GLC) yield of benzyl alcohol was also obtained.

EXPERIMENTAL PART

General.- For general information see, for instance, reference 10aa. Starting sulfones **1a**[15], **1b**[16], **1c**[17], **1d**[18] were prepared by reaction of the corresponding alkyl bromides with sodium benzenesulfinate in methanol[12]. Sulfones **1e**[19] and **1f**[20] were prepared by hydrogen peroxide oxidation of the corresponding sulfide[19] and by a tandem iodosulfonylation-elimination of cyclohexene[21], respectively. Starting sulfoxides **6b**[22], **6c**[23], **6d**[24] and **6e**[25] were prepared from the corresponding sulfides (obtained by reaction of benzenethiol with the corresponding alkyl bromide in the presence of sodium ethoxide)[26] by sodium periodate oxidation[27].

Naphthalene-Catalysed Lithiation of Alkyl Phenyl Sulfones **1**. *Isolation of Compounds* **2**. *General Procedure*.- To a green suspension of lithium powder (100 mg, 14 mmol) and naphthalene (20 mg, 0.16 mmol) in THF (5 ml) was added a solution of the corresponding sulfone **1** (1 mmol) and the electrophile (1.2 mmol) [and $BF_3\cdot OEt_2$ (2.2 mmol) for starting sulfones **1a**, and **1b** or **1d** in the reaction with benzaldehyde or cyclohexanone; see Table 1, entries 1-3, 8 and 10, and footnote d] in THF (4 ml) at -78°C (-30°C for compound **1c**) under argon for 15 min. Stirring was continued for 5 additional h allowing the temperature to rise till 20°C. The resulting mixture was then hydrolysed with water (5 ml), extracted with diethyl ether (2x20 ml) and the organic layer dried over anhydrous Na_2SO_4. Solvents were evaporated (15 Torr) and the resulting residue was chromatographied (silica gel, hexane/ethyl acetate) to afford pure title compounds **2**. In the case of using $BF_3\cdot OEt_2$ as co-reagent the final hydrolysis was carried out with 2 N HCl and extracted with diethyl ether. The organic layer was successively washed with 2 N NaOH (2x10 ml) and water (2x10 ml) and dried and purified as above. Yields and R_f values are included in Table 1. Products **2aa**[10r,28], **2ab**[10r,29], **2ba**[10d,30], **2bb**[10d,31], **2ca**[10r,32], **2cb**[10r,33], **2da**[10d,34], **2db**[10d,35], **2dc**[10d,36], **2dd**[10d,37], **2de**[10y,38] as well as by-products **2'ab**[10t,39], **2'bb**[40] and **2'cb**[41] were fully characterised by their physical, chromatographic and spectroscopic data in comparison to those described by us[10] and others[28-41] in the literature.

Naphthalene-Catalysed Lithiation of Sulfolene (**3**). *Isolation of Compounds* **5**. *General procedure*. - The reaction was carried out as it was above described for the transformation **1**→**2** (Scheme 1) using a 1 mmol scale (sulfolene/electrophile molar ratio: 1/2). Yields, diastereoisomers ratio and R_f values are included in Table 2; physical, spectroscopic and analytical data follow.

5-Isopropyl-4-vinyl-1,2-oxathiolane S-*Oxide* (**5a**): Major diastereoisomer (R_f 0.66; Table 2): t_r 9.22 min; ν (film) 3050, 3010, 1635 (HC=C) and 1120 cm^{-1} (SO); δ_H 1.03, 1.04 (3 H each, 2 d, *J*=6.7 and 7.0 Hz, respectively, 2xMe), 1.97-2.08 (1 H, m, C*H*Me), 2.83 (1 H, t, *J*=12.2 Hz, C*H*HS), 3.12 (1 H, dd, *J*=12.2, 5.8 Hz, C*H*HS), 3.47-3.54 (1 H, m, $C\mathit{H}CH_2S$), 4.10 (1 H, dd, *J*=9.7, 4.8 Hz, CHO), 5.23 (1 H, dt, *J*=10.1, 0.8 Hz, C*H*H=C), 5.30 (1 H, dt, *J*=17.1, 0.8 Hz, C*H*H=C) and 5.68 (1 H, ddd, *J*=17.1, 10.1, 8.2 Hz, $C\mathit{H}$=CH_2); δ_C 17.55, 19.95 (2xMe), 31.65 (*C*HMe), 43.6 ($\mathit{C}HCH_2S$), 63.45 (CH_2S), 98.35 (CO), 119.3 ($\mathit{C}H_2$=C) and 134.5 ($\mathit{C}H$=CH_2); *m/z* 174 (M^+, 3 %), 109 (42), 102 (50), 95 (19), 87 (10), 85 (14), 83 (11), 81 (16), 69 (15), 68 (23), 67 (34), 56 (63), 55 (40), 54 (100), 53 (33), 51 (13), 48 (11), 45 (10), 43 (75) and 41 (98). Second diastereoisomer (R_f 0.62; Table 2): t_r 9.59 min; ν (film) 3050, 3020, 1640 (HC=C) and 1125 cm^{-1} (SO); δ_H 0.96, 1.08 (3 H each, 2 d, *J*=6.7 Hz each, 2xMe), 1.87-2.00 (1 H, m, C*H*Me), 3.05 (1 H, dd, *J*=13.4, 7.0 Hz, C*H*HS), 3.25-3.35 (1 H, m, $C\mathit{H}CH_2S$), 3.45 (1 H, dd, *J*=13.4, 2.8 Hz, C*H*HS), 4.61 (1 H, dd, *J*=9.5, 4.6 Hz, CHO), 5.11-5.19 (2 H, m, CH_2=C) and 5.68 (1 H, ddd, *J*=17.1, 10.4, 9.5 Hz, $C\mathit{H}$=CH_2); δ_C 18.85, 19.85 (2xMe), 28.7 (*C*HMe), 45.15 ($\mathit{C}HCH_2S$), 67.3 (CH_2S), 93.2 (CO), 118.05 ($\mathit{C}H_2$=C) and 133.95 ($\mathit{C}H$=CH_2); *m/z* 174 (M^+, 4 %), 102 (47), 95 (11), 85 (18), 68 (18), 67 (27), 56 (48), 55 (30), 54 (100), 53 (26), 51 (10), 48 (10), 43 (59) and 41 (73).

5,5-Dimethyl-4-vinyl-1,2-oxathiolane S-*Oxide* (**5b**): Major diastereoisomer (R_f 0.27; Table 2): t_r 8.12 min; ν (film) 3070, 1640 (HC=C) and 1110 cm^{-1} (SO); δ_H 1.16, 1.61 (3 H each, 2 s, 2xMe), 3.03 (1 H, t, *J*=12.5 Hz, C*H*HS), 3.11 (1 H, dd, *J*=12.5, 6.1 Hz C*H*HS), 3.53 (1 H, dddt, *J*=12.5, 8.2, 6.1, 0.9 Hz, $C\mathit{H}CH_2S$), 5.26 (1 H, ddd, *J*=10.1, 1.2, 0.6 Hz, C*H*H=C), 5.30 (1 H, dt,*J*=17.1, 1.2 Hz, C*H*H=C) and 5.72 (1 H, ddd, *J*=17.1, 10.1, 8.2 Hz, $C\mathit{H}$=CH_2); δ_C 23.8, 29.75 (2xMe), 49.05 ($\mathit{C}HCH_2S$), 61.45 (CH_2S), 96.05 (CO), 119.4 ($\mathit{C}H_2$=C) and 132.65 ($\mathit{C}H$=CH_2); *m/z* 162 (M^++2, 1%), 161 (M^++1, 2), 160 (M^+, 16), 106 (25), 102 (38), 96 (13), 95 (10), 85 (21), 81 (100), 79 (28), 67 (12), 55 (10), 54 (53), 53 (19), 43 (39) and 41 (17) (Found: M^+, 160.0563. $C_7H_{12}O_2S$ requires M, 160.0558).

5,5-Diethyl-4-vinyl-1,2-oxathiolane S-*Oxide* (**5c**): Major diastereoisomer (R_f 0.40; Table 2): t_r 10.46 min; ν (film) 3060, 1630 (HC=C) and 1120 cm^{-1} (SO); δ_H 0.93 (3 H, t, *J*=7.4 Hz, Me), 1.00 (3 H, dd, *J*=7.8, 7.3 Hz, Me), 1.50 (2 H, q, *J*=7.4 Hz, 2xC*H*HMe), 1.77-1.98 (2 H, m, 2xC*H*HMe), 3.04-3.07 (2 H, m, CH_2S), 3.60-3.64 (1 H, m, $C\mathit{H}CH_2S$), 5.21-5.28 (2 H, m, CH_2=C) and 5.77 (1 H, ddd, *J*=17.1, 10.1, 8.1 Hz, $C\mathit{H}$=CH_2); δ_C 7.7, 8.3 (2xMe), 27.65, 30.6 (2xCH_2Me), 46.3 ($\mathit{C}HCH_2S$), 61.95 (CH_2S), 100.75 (CO), 119.05 ($\mathit{C}H_2$=C) and 133.1 ($\mathit{C}H$=CH_2); *m/z* 188 (M^+, 2 %), 134 (10), 123 (11), 103 (11), 102 (12), 95 (42), 87 (15), 85 (16), 81 (17), 70 (11), 69 (20), 67 (31), 57 (100), 55 (39), 54 (73), 53 (26), 48 (10), 45 (22), 43 (16) and 41 (42) (Found: M^+, 188.0869. $C_9H_{16}O_2S$ requires M, 188.0871). Minor diastereoisomer (R_f 0.29;

Table 2): t_r 10.40 min; ν (film) 3070, 1635 (HC=C) and 1125 cm^{-1} (SO); δ_H 0.92 (3 H, t, *J*=7.6 Hz, Me), 1.01 (3 H, t, *J*=7.4 Hz, Me), 1.47-1.91, 2.01-2.13 (3 H and 1 H, respectively, 2 m, 2x$C\mathit{H}_2$Me), 2.97-3.08 (2 H, m, CH_2S), 3.61-3.71 (1 H, m, $C\mathit{H}CH_2S$), 5.14 (1 H, d, *J*=16.9 Hz, C*H*H=C), 5.16 (1 H, d, *J*=10.3 Hz, CH*H*=C) and 5.99 (1 H, ddd, *J*=16.9, 10.3, 8.5 Hz, $C\mathit{H}{=}CH_2$); δ_C 7.75, 8.15 (2xMe), 28.45, 28.8 (2x$\mathit{C}H_2$Me), 50.85 ($\mathit{C}HCH_2S$), 64.95 (CH_2S), 101.6 (CO), 118.3 ($\mathit{C}H_2{=}C$) and 134.95 ($\mathit{C}H{=}CH_2$); *m/z* 188 (M$^+$, 1 %), 134 (11), 123 (12), 103 (11), 102 (12), 95 (42), 85 (15), 81 (13), 70 (10), 69 (20), 67 (35), 57 (100), 55 (31), 54 (47), 53 (19), 43 (10) and 41 (27) (Found: M$^+$, 188.0879. $C_9H_{16}O_2S$ requires M, 188.0871).

4-Vinyl-1-oxa-2-thiaspiro[4, 4]nonane S-Oxide (**5d**): Major diastereoisomer (*R$_f$* 0.35; Table 2): t_r 11.10 min; ν (film) 3060, 1635 (HC=C) and 1130 cm^{-1} (SO); δ_H 1.56-1.97 (8 H, m, 4xCH_2 ring), 3.00 (1 H, t, *J*=12.2 Hz, C*H*HS), 3.12 (1 H, dd, *J*=12.2, 5.8 Hz, CH*H*S), 3.63 (1 H, dddt, *J*=12.2, 8.4, 5.8, 0.9 Hz, $C\mathit{H}CH_2S$), 5.25 (1 H, ddd, *J*=10.1, 1.2, 0.6 Hz, C*H*H=C), 5.27 (1 H, dt, *J*=17.0, 1.2 Hz, CH*H*=C) and 5.72 (1 H, ddd, *J*=17.0, 10.1, 8.4 Hz, $C\mathit{H}{=}CH_2$); δ_C 23.05, 23.9, 34.1, 39.05 (4xCH_2 ring), 46.3 ($\mathit{C}HCH_2S$), 62.4 (CH_2S), 106.05 (CO), 119.2 ($\mathit{C}H_2{=}C$) and 133.0 ($\mathit{C}H{=}CH_2$); *m/z* 187 (M$^+$+1, 1%), 186 (M$^+$, 8), 132 (36), 122 (12), 121 (62), 107 (30), 102 (33), 94 (18), 93 (91), 92 (10), 91 (32), 87 (11), 85 (27), 84 (18), 81 (59), 80 (28), 79 (100), 77 (32), 68 (33), 67 (66), 65 (13), 56 (10), 55 (40), 54 (55), 53 (30), 51 (12) and 41 (27) (Found: M$^+$, 186.0717. $C_9H_{14}O_2S$ requires M, 186.0714).

4-Vinyl-1-oxa-2-thiaspiro[4, 5]decane S-Oxide (**5e**): Major diastereoisomer (*R$_f$* 0.38; Table 2): t_r 12.10 min; ν (film) 3060, 1635 (HC=C) and 1115 cm^{-1} (SO); δ_H 1.15-1.81 (10 H, m, 5xCH_2 ring), 2.72 (1 H, q, *J*=8.9 Hz, $C\mathit{H}CH_2S$), 3.03, 3.73 (1 H each, 2 dd, *J*=13.4, 8.9 Hz each, CH_2S), 5.15 (1 H, dt, *J*=17.0, 1.2 Hz, C*H*H=C), 5.19 (1 H, ddd, *J*=10.1, 1.5, 0.6 Hz, CH*H*=C) and 5.93 (1 H, ddd, *J*=17.0, 10.1, 8.9 Hz, $C\mathit{H}{=}CH_2$); δ_C 21.75, 22.8, 25.25, 33.35, 36.8 (5xCH_2 ring), 54.4 ($\mathit{C}HCH_2S$), 64.65 (CH_2S), 98.65 (CO), 118.65 ($\mathit{C}H_2{=}C$) and 134.5 ($\mathit{C}H{=}CH_2$); *m/z* 201 (M$^+$+1, 1 %), 200 (M$^+$, 4), 146 (29), 135 (34), 121 (12), 107 (25), 102 (32), 99 (10), 98 (17), 95 (10), 94 (18), 93 (21), 91 (17), 85 (10), 82 (36), 81 (91), 80 (18), 79 (60), 77 (20), 69 (24), 68 (22), 67 (100), 65 (12), 55 (64), 54 (81), 53 (36), 51 (12), 43 (14), 42 (31) and 41 (62) (Found: M$^+$, 200.0871. $C_{10}H_{16}O_2S$ requires M, 200.0871). Minor diastereoisomer (*R$_f$* 0.35; Table 2): t_r 12.15 min; ν (film) 3060, 1635 (HC=C) and 1115 cm^{-1} (SO); δ_H 1.16-1.93 (10 H, m, 5xCH_2 ring), 2.98-3.13 (2 H, m, CH_2S), 3.39 (1 H, ddd, *J*=12.5, 8.4, 6.3 Hz, $C\mathit{H}CH_2S$), 5.22-5.28 (2 H, m, $CH_2{=}C$) and 5.71 (1 H, ddd, *J*=17.0, 10.1, 8.4 Hz, $C\mathit{H}{=}CH_2$); δ_C 21.3, 22.85, 25.1, 32.7, 38.5 (5xCH_2 ring), 49.65 ($\mathit{C}HCH_2S$), 61.05 (CH_2S), 97.55 (CO), 119.05 ($\mathit{C}H_2{=}C$) and 133.15 ($\mathit{C}H{=}CH_2$); *m/z* 202 (M$^+$+2, 1 %), 201 (M$^+$+1, 2), 200 (M$^+$, 9), 146 (64), 136 (15), 135 (93), 121 (27), 108 (10), 107 (37), 102 (64), 99 (15), 98 (30), 95 (19), 94 (24), 93 (43), 91 (20), 85 (19), 82 (51), 81 (96), 80 (28), 79 (67), 77 (22), 69 (25), 68 (19), 67 (100), 65 (10), 55 (46), 54 (65), 53 (27), 43 (10), 42 (18) and 41 (40) (Found: M$^+$, 200.0858. $C_{10}H_{16}O_2S$ requires M, 200.0871).

Arene-Catalysed Lithiation of Alkyl Phenyl Sulfoxides **6**. *Isolation of Compounds* **2**. *General Procedure*.- To a green suspension of lithium powder (100 mg, 14 mmol) and naphthalene (20 mg, 0.16 mmol) in THF (5 ml) was added a solution of the corresponding sulfoxide **6** (1 mmol) and the electrophile (1.2 mmol) in THF (2 ml) at -78°C under argon for 5 min. Stirring was continued for 5 additional h allowing the temperature to rise till 20°C. In the case of using DTBB (26 mg, 0.1 mmol) as the catalyst, the addition time ranged between 25 and 45 min[42] at 0°C allowing then the temperature to rise till 20°C for 1 additional h. In both cases the work-up was the same as it was above described for the tranformation **1**→**2**. Reaction conditions[42], yields and *R$_f$* values are included in Table 3. Products **2ba**, **2ca**, **2da**, **2db** and **2dc** gave the same physical and spectroscopic data as the corresponding ones obtained from sulfones **1** (compare Tables 1 and 3); products **2bc**[10d,43], **2ea**[10r,28] and **2eb**[10r,44] as well as by-products (benzyl alcohol and dihenyl carbinol)[45] were fully characterised by comparison of their physical and spectroscopic data with those described in the literature.

ACKNOWLEDGEMENTS

This work was supported by DGICYT of Spain (no. PB91-0751). D. G. thanks the Conselleria de Cultura, Educació i Ciencia de la Generalitat Valenciana for a fellowship.

REFERENCES AND NOTES

1. (a) Houben-Weyl *Organische Schwefel-Verbindungen*, Band E11; Klamann, D., Ed.; G. Thieme Verlag: Stuttgart, 1985. (b) *The Chemistry of Sulfones and Sulfoxides*; Patai, S.; Rappoport, Z.; Stirling, C. J. M., Eds; J. Wiley & Sons: Chichester, 1988.
2. Simpkins, N. S. *Sulfones in organic Chemistry*; Pergamon Press: Oxford, 1993.
3. The other common procedure for eliminating the sulfone moiety consists in a sulfinate β-elimination giving olefins. See, for instance, reference 2, chapter 7.
4. (a) Sodium/liquid ammonia: Marshall, J. A.; Cleary, D. G. *J. Org. Chem.* **1986**, *51*, 858-863. (b) Lithium/ethylamine: Truce, W. E.; Frank, F. J. *J. Org. Chem.* **1967**, *32*, 1918-1920. Paquette, L. A.; Fischer, J. W.; Browne, A. R.; Doecke, C. W. *J. Am. Chem. Soc.* **1985**, *107*, 686-691. Hutchinson, D. K.; Fuchs, P. L. *J. Am. Chem. Soc.* **1987**, *109*, 4755-4756. (c) Soodium amalgam/ethanol: Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3477-3478. Anderson, M. B.; Ranasinghe, M. G.; Palmer, J. T.; Fuchs, P. L. *J. Org. Chem.* **1988**, *53*, 3125-3127. (d) Potassium/toluene: Chou, T.; You, M.-L. *Tetrahedron Lett.* **1985**, *26*, 4495-4498. Chou, T.; You, M.-L. *J. Org. Chem.* **1987**, *52*, 2224-2226. Chou, T.; Hung, S.-H.; Peng, M.-L.; Lee, S.-J. *Tetrahedron Lett.* **1991**, *32*, 3551-3554.
5. Other methodologies for the reductive desulfonylation of alkyl aryl sulfones involving different reagents than metals in solution, are, for instance: (a) SmI$_2$: Kende, A. S.; Mendoza, J. S. *Tetrahedron Lett.* **1990**, *31*, 7105-7108. Künzer, H.; Stahnke, M.; Sauer, G.; Wiechert, R. *Tetrahedron Lett.* **1991**, *32*, 1949-1952. (b) LiAlH$_4$: Dufort, N.; Jodoin, B. *Can. J. Chem.* **1978**, *56*, 1779-1781. (c) LiAlH$_4$/Ni-reagent: Becker, S.; Fort, Y.; Caubère, P. *J. Org. Chem.* **1990**, *55*, 6194-6198. Chan, M.-C.; Cheng, K.-M.; Ho, K. M.; Ng, C. T.; Yam, T. M.; Kang, B. S. L.; Luh, T.-Y. *J. Org. Chem.* **1988**, *53*, 4466-4471. Ho, K. M.; Lam, C. H.; Luh, T.-Y. *J. Org. Chem.* **1989**, *54*, 4474-4476. (d) Photolysis: Cheng, C.; Stock, L. M. *J. Org. Chem.* **1991**, *56*, 2436-2443. (e) Electrolysis: Lamm, B. *Tetrahedron Lett.* **1972**, 1469-1470. Lamm, B.; Nilsson, A. *Acta Chem. Scand., B* **1983**, *37*, 77-78.
6. For a recent sulfone/lithium exchange in *gem*-disulfones, see: (a) Yu, J.; Cho, H.-J.; Falck, J. R. *J. Org. Chem.* **1993**, *58*, 5892-5894. (b) Yu, J.; Cho, H.-J.; Chandrasekhar, S.; Falck, J. R.; Miokowski, C. *Tetrahedron Lett.* **1994**, *35*, 5437-5440.
7. For an example of preparing a lithium enolate from a α-sulfonyl carbonyl compound by treatment with lithium naphthalenide, see: Beau, J.-M.; Sinaÿ, P. *Tetrahedron Lett.* **1985**, *26*, 6193-6195.
8. For β-elimination of β-ketosulfoxides promoted by metals and amalgams in solution (SET-process) see, for instance: Caubère, P.; Coutrot, P. In *Comprehensive Organic Synthesis*; Trost, B.; Fleming, I., Eds.; Pergamon Press: Oxford, 1991; vol. 8, pp. 842-845.
9. Yus, M.; Ramón, D. J. *J. Chem. Soc., Chem. Commun.* **1991**, 398-400.
10. For other arene-catalysed lithiation from our laboratory, see: (a) Yus, M.; Ramón, D. J. *J. Org. Chem.* **1992**, *57*, 750-751. (b) Yus, M.; Ramón, D. J. *Tetrahedron Lett.* **1992**, *33*, 2217-2220. (c) Ramón, D. J.; Yus, M. *Tetrahedron* **1992**, *48*, 3585-3588. (d) Guijarro, D.; Mancheño, B.; Yus, M. *Tetrahedron* **1992**, *48*, 4593-4600. (e) Guijarro, D.; Mancheño, B; Yus, M. *Tetrahedron Lett.* **1992**, *33*, 5597-5600. (f) Guijarro, A.; Ramón, D. J.; Yus, M. *Tetrahedron* **1993**, *49*, 469-482. (g) Guijarro, D.; Mancheño, B.; Yus, M. *Tetrahedron* **1993**, *49*, 1327-1334. (h) Almena, J.; Foubelo, F.; Yus, M. *Tetrahedron Lett.* **1993**, *34*, 1649-1652. (i) Guijarro, A.; Yus, M. *Tetrahedron Lett.* **1993**, *34*, 2011-2014. (j) Gómez, C.; Ramón, D. J.; Yus, M. *Tetrahedron* **1993**, *49*, 4117-4126. (k) Gil, J. F.; Ramón, D. J.; Yus, M. *Tetrahedron* **1993**, *49*, 4923-4938. (l) Guijarro, A.; Yus, M. *Tetrahedron Lett.* **1993**, *34*, 3487-3490. (m) Guijarro, D.; Yus, M. *Tetrahedron* **1993**, *49*, 7761-7768. (n) Gil, J. F.; Ramón, D. J.; Yus, M. *Tetrahedron* **1993**, *49*, 9535-9546. (o) Ramón, D. J.; Yus, M. *Tetrahedron* **1993**, *49*, 10103-10110. (p) Ramón, D. J.; Yus, M. *Tetrahedron Lett.* **1993**, *34*, 7115-7118. (q) Guijarro, A.; Yus, M. *Tetrahedron Lett.* **1994**, *35*, 253-256. (r) Guijarro, D.; Guillena, G.; Mancheño, B.; Yus, M. *Tetrahedron* **1994**, *50*, 3427-3436. (s) Gil, J. F.; Ramón, D. J.; Yus, M. *Tetrahedron* **1994**, *50*, 3437-3446. (t) Guijarro, D.; Yus, M. *Tetrahedron* **1994**, *50*, 3447-3452. (u) Almena, J.; Foubelo, F.; Yus, M. *Tetrahedron* **1994**, *50*, 5775-5782. (v) Gil, J. F.; Ramón, D. J.; Yus, M. *Tetrahedron* **1994**, *50*, 7307-7314. (w) Almena, J.; Foubelo, F.; Yus, M. *J. Org. Chem.* **1994**, *59*, 3210-3215. (x) Guijarro, A.; Yus, M. *Tetrahedron* **1994**, *50*, 7857-7864. (y) Guijarro, D.;

Mancheño, B; Yus, M. *Tetrahedron* **1994**, *50*, 8551-8558. (z) Bachki, A.; Foubelo, F.; Yus, M. *Tetrahedron Lett.* **1994**, *35*, 7643-7646. (aa) Guijarro, A.; Yus, M.*Tetrahedron* **1994**, *50*, 13269-13276:

11. For a preliminary communication, see: Guijarro, D.; Yus, M. *Tetrahedron Lett.* **1994**, *35*, 2965-2968.
12. Trost, B. M.; Schmuff, N. R. *J. Am. Chem. Soc.* **1985**, *107*, 396-405.
13. We found these conditions to be the best ones. As an example, the results for the reaction of sulfone **1a** with benzaldehyde (compare to Table 1, entry 1) are included in the following table:

Arene (mol%)	$C_{10}H_8$(8)	$C_{10}H_8$(8)	$C_{10}H_8$(8)	DTBB(5)	DTBB(5)	DTBB(5)
T (°C)	0	-30	-78	0	-30	-78
Yield (%)	35	40	46	27	22	20

14. This yield refers to the following stoichiometry: DMS → 2MeLi → 2PhCH(OH)Me.
15. Reddy, R. S.; Reddy, J. S.; Kumar, R.; Kumar, P. *J. Chem. Soc., Chem. Commun.* **1992**, 84-85.
16. Kamigata, N.; Ishii, K.; Ohtsuka, T.; Matsuyama, H. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3479-3481; *Chem. Abstr.* **1992**, *117*, 26001k.
17. Cabiddu, M. G.; Cabiddu, S.; Fattuoni, C.; Floris, C.; Gelli, G.; Melis, S. *Synthesis* **1993**, 41-42.
18. Shriner, R. L.; Struck, H. C.; Jorison, W. J. *J. Am. Chem. Soc.* **1930**, *52*, 2060-2069.
19. Brace, N. O. *J. Org. Chem.* **1993**, *58*, 4506-4508.
20. Kim, K. S.; Kim, T. K.; Hahn, C. S. *Taehan, Hwahakhoe Chi* **1989**, *33*, 677-678; *Chem. Abstr.* **1990**, *113*, 5812c.
21. Inomata, K.; Kobayashi, T.; Sasaoka, S.; Kinoshita, H.; Kotake, H. *Chem. Lett.* **1986**, 289-292.
22. Hojo, M.; Masuda, R. *Tetrahedron Lett.* **1976**, 613-614.
23. Drabowicz, J.; Mikolajczyk, M. *Synthesis* **1976**, 527-528.
24. Kingsbury, C. A. *J. Org. Chem.* **1972**, *37*, 102-105.
25. Wudl, F.; Lee, T. B. K. *J. Am. Chem. Soc.* **1973**, *95*, 6349-6358.
26. Paquette, L. A.; Carr, R. V. C. *Organic Synthesis*, Coll. Vol. VII, 453-456.
27. Leonard, N. J.; Johnson, C. R. *J. Org. Chem.* **1962**, *27*, 282-284.
28. Noyori, R.; Tonaino, I.; Tanimoto, Y. *J. Am. Chem. Soc.* **1979**, *101*, 3129-3131.
29. Bergmann, E.; Blum-Bergmann, O. *J. Am. Chem. Soc.* **1937**, *59*, 1572-1573.
30. Akiyama, S.; Mooz, J. *Tetrahedron Lett.* **1973**, 4115-4118.
31. Katzenellenbogen, J. A.; Lenox, R. S. *J. Org. Chem.* **1973**, *38*, 326-335.
32. McLeod, R.; Welch, F. J.; Mosher, H. S. *J. Am. Chem. Soc.* **1960**, *82*, 876-880.
33. Servis, K. L.; Bowler, D. J.; Ishii, C. *J. Am. Chem. Soc.* **1975**, *97*, 73-80.
34. Fry, A. J.; Bujanauskas, J. P. *J. Org. Chem.* **1978**, *43*, 3157-3163.
35. Berti, G.; Bottari, F.; Ferrarini, P. L.; Machia, B. *J. Org. Chem.* **1965**, *30*, 4091-4096.
36. Kropf, H.; Bernert, C. R. *Justus Liebigs Ann. Chem.* **1971**, *751*, 109-120.
37. Huang, Y.; Liao, Y.; Chen, C. *J. Chem. Soc., Chem. commun.* **1990**, 85-86.
38. Tzeng, D.; Weber, W. P. *J. Org. Chem.* **1981**, *46*, 265-267.
39. Baddeley, G.; Chadnick, J.; Taylor, H. T. *J. Chem. Soc.* **1956**, 448-450.
40. Inman, W. D.; Sánchez, K. A. J.; Chaidez, M. A.; Paulson, D. R. *J. Org. Chem.* **1989**, *54*, 4872-4881
41. Mandai, T.; Suzuki, S.; Murakami, T.; Fujita, M.; Kamada, M.; Tsuji, J. *Tetrahedron Lett.* **1992**, *33*, 2987-2990.
42. Addition times corresponding to the preparation of compounds **2** from sulfoxides **6** using DTBB as the catalyst are: **2ea**/35 min, **2eb**/25 min and **2ca**/45 min.
43. Huet, J. *Bull. Soc. Chim. Fr.* **1964**, *10*, 2677-2680.
44. Vaida, M. S.; Dikii, M. A. *Visu. L'viv. Politekh. Inst.* **1977**, *112*, 5-8; *Chem. Abstr.* **1977**, *87*, 200985h.
45. *Aldrich Catalogue Handbook of Fine Chemical*; Aldrich-Chemie GmbH & Co. KG: Steinheim, 1994.

(*Received in UK* 8 *December* 1994; *accepted* 21 *December* 1994)