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SYNTHESES WITH SULFONES XLVI : STEREOSELECTIVE PREPARATION OF 2- BENZENESULFONYL-1,3-DIENES AND 2-BENZENESULFONYL-1,4-DIENES

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Abstract : The stereoselective syntheses of EE 2-benzenesulfonyl-1,3-dienes and 2-benzenesulfonyl-1,4-dienes are described. Diels-Alder cycloaddition of the EE 2-benzenesulfonyl-1,3-dienes 3b with methylvinyketone is reported.

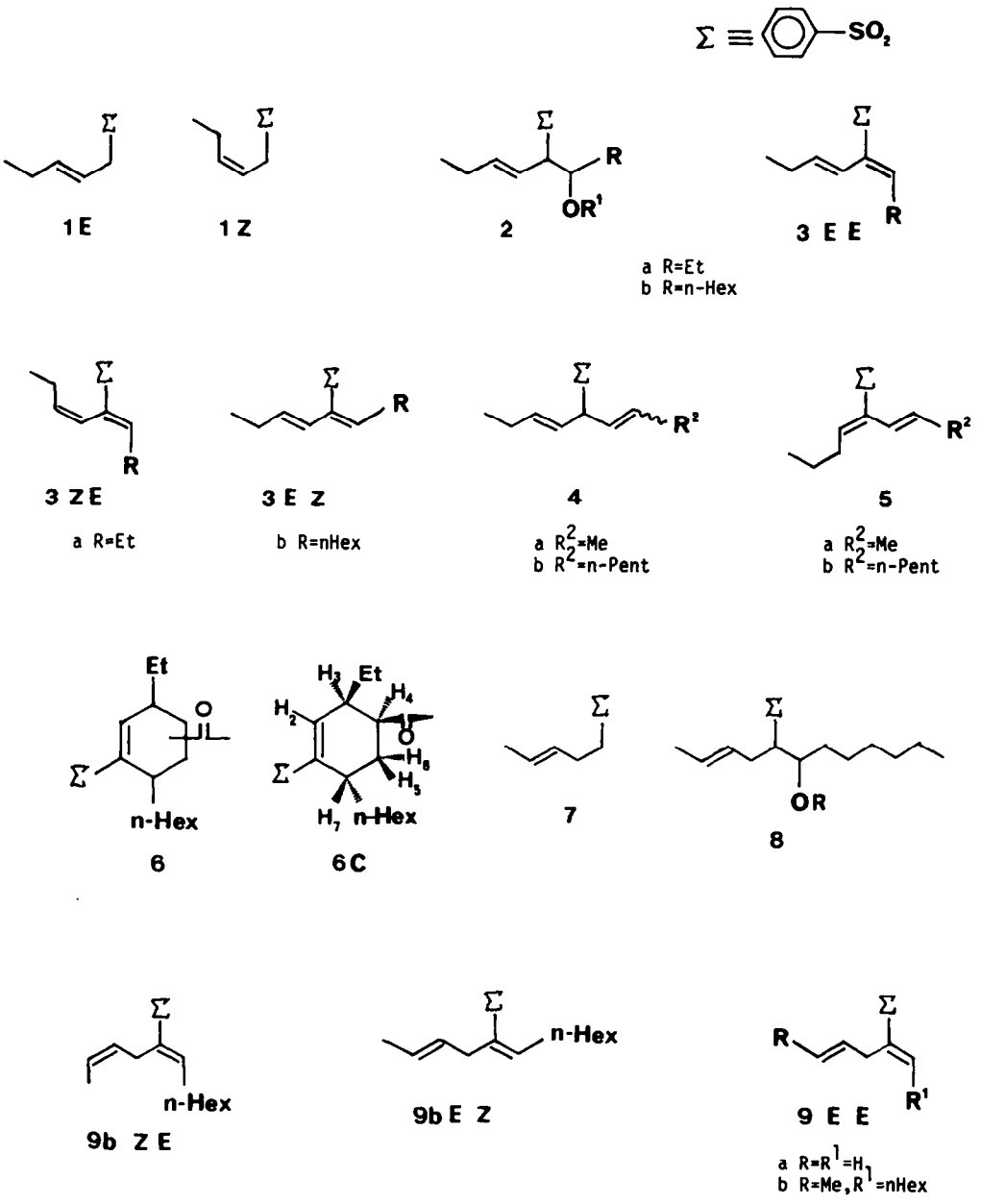
In a new way to prepare Z olefins, recently described, acetoxysulfones (threo and erythro) are formed by condensation of aldehydes with metalated sulfones ; acetic acid is eliminated to give E vinylic sulfones [1] which in turn are converted into Z olefins by stereospecific hydrogenolysis with sodium dithionite[2] or Grignard reagents under transition-metal catalysis[3]. Threo tosyloxysulfones are converted into Z vinylic sulfones and then E olefins in a similar manner[1,2]. We reported our preliminary results in EZ 1,3-diene synthesis using this method[4]. Full details of the stereoselective preparation of both 2- benzenesulfonyl 1,3- and 1,4-dienes are given here as well as some aspects of the reactivity of the former. The stereospecific reduction of the sulfonyl group and applications to pheromone synthesis are presented in the following paper [5].

2-Benzenesulfonyl-1,3-dienes

In order to prepare 2-benzenesulfonyl 1,3-dienes, readily available E 1-benzenesulfonyl 2-pentene 1[6] was treated first with n-butyllithium and then with aldehydes. The reaction mixture was quenched with acetic anhydride according to the technique recommended for preparing E vinysulfones[1]. Workup yielded 78-9 % of a 55/45 mixture of threo and erythro compounds 2 R^1=Ac identified by ^{1}H NMR from the coupling constants of the α -sulfonyl proton [7], Table 1, entries 1 and 2. Acetylation was not always complete under these conditions and significant amounts (18 %) of hydroxysulfones have been detected, entry 3. When the reaction mixture was quenched at -35°C with a saturated solution of ammonium chloride followed by workup and acetylation[8] in a second step (the technique recommended (vide supra) for preparing 2 R^1=Ac) 63 % of the acetoxysulfones were obtained, entry 4.

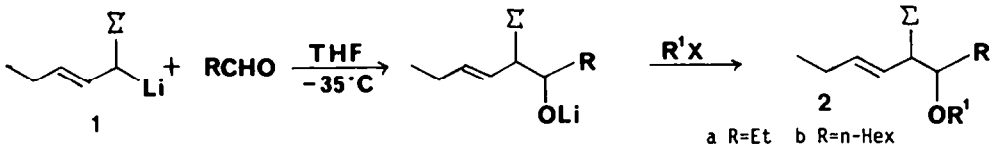
In order to establish the olefinic purity of diene sulfones 3 , threo 2b R^1=Ts, the precursor for 3b EZ[1], and an E/Z mixture of acetoxysulfones 2b E+Z, R^1=Ac,precursors for a mixture of 3b EE and 3b ZE, were required. Thus quenching the reaction with tosyl chloride led to a mixture of threo/erythro hydroxysulfones (45/55) in 24 % yield together with pure threo tosylate 2b, R=n-Hex, R^1=Ts (29 %), entry 5. Some dienesulfones (18 % 3b EE and 7 % 3b EZ) were also found which points to a much easier elimination from the erythro tosylate than from the threo isomer. The E/Z mixture of β-acetoxysulfones 2b was obtained in modest yield, 50%, entry 6. β-Functionalized allylic sulfones 2 were then exposed to the basic conditions used in the synthesis of E and Z vinylic sulfones[1], Table 2. Stirring acetoxysulfones 2aE with powdered sodium

FORMULAE



hydroxide in dioxane at room temperature for 4h yielded 67 % of mainly one isomer of dienesulfone 3a, entry 1. Basic equilibration of 3a to isomers 4a and 5a, identified by ^{1}H NMR(see experimental part), was limited to 10 % after 6h but substantial, 35 %, under the basic conditions used during a prolonged experiment, entry 2. It should be noted that significant amounts of bisallylsulfones 4b E+Z, easily separated by tlc, were also formed in eliminations from mixtures of hydroxysulfones 2b R^1=H and acetoxysulfones 2b R^1=Ac, entries 3 and 4, as well as in eliminations performed in ethanol, entries 6 and 7. The undesired regioisomer 4 could not be detected in the product obtained when acetoxysulfones, 2b R^1=Ac, prepared in two steps (see Table 1, entry 4), were treated with two equivalents of sodium hydroxide in ether for 3h. Under these conditions, which we recommend for eliminating acetic acid from compounds 2b R^1=Ac, 75 % of a 94/6 mixture of

TABLE 1 : Condensation of lithiated sulfone 1 with aldehydes followed by reaction of alkoxide ion with electrophiles



a R=Et b R=n-Hex

Entry	1 % Z[a]	R	R^1X	Major Products 2[b] (Yield %)	Diastereoisomer Ratio Number	threo/erythro	Minor Products %
1	2	Et	Ac_2O	2a, R^1=Ac (79)	2	55/45	1[b]
2	0.3	nHex	"	2b, R^1=Ac (78)	2	"	1[b]
3	0.5	"	"	2b, R^1=Ac (56) 2b, R^1=H (18)	2	"	
4	0.5	"	1.NH_4Cl[c] 2.Ac_2O DMAP	2b, R^1=Ac (63)	2	60/40	
5	1	"	TsCl	2b, R^1=Ts (29)	1	100/0	1[b]
				2b, R^1=H (24)	2	45/55	3b EE 18 % 3b EZ 7 %
6	18	"	Ac_2O	2b, R^1=Ac (50)[d]	4	n.d.	25% by weight of unidentified sulfones

[a] hplc ; [b] capillary-VPC indicated ~5 % of unreacted 1 ; [c] hydrolysis at -35 °C ; acetylation according to ref. 8 ; [d] 10 % of 1 was recovered after elimination of AcOH from 2b, R^1=Ac, Table 2 entry 9.

dienesulfones 3bEE and 3bEZ were obtained. Flash chromatography of the crude product afforded dienesulfone 3bEE > 99 % pure according to hplc (±0.5 %). On the other hand threo tosyloxysulfone 2b R^1=Ts yielded 78 % of a 88/12 mixture of dienesulfones 3bEZ and 3bEE under conditions used for preparing Z vinylsulfones [1], entry 8. Again the major isomer, this time 3bEZ, was obtained > 99 % pure by Flash Chromatography. It thus proved possible to obtain both isomers in a state of high stereochemical purity. Finally, elimination from an E/Z mixture of 2b R^1=Ac furnished 39 % of dienesulfones 3b, entry 9. Although only two signals in a 98/2 ratio were observed by hplc analysis, 11 % of the 3bZE isomer was detected by ^1H NMR.

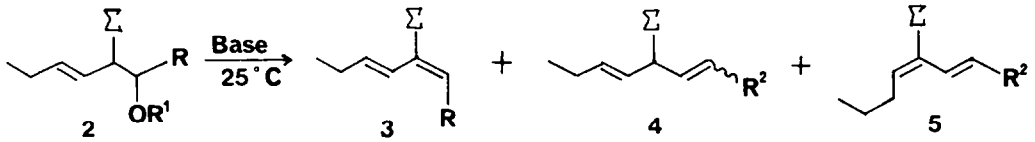
It should be noted that the reaction of β-acetoxysulfones under alkaline conditions is strongly influenced by the choice of the basic reagent. Otera and coll[9] recently reported formation of enyne, diyne and polyene compounds with t-BuOK in THF or tBuOH. Stereoequilibration of dienesulfones 3 by I_2[10] or Br_2[11] proved unsatisfactory due to formation of unidentified sulfones, probably addition products. Prolonged equilibration of vinylsulfones with Br_2 has been reported to lead to addition products[11].

The Diels-Alder reaction of 2-phenylsulfonyl-1,3-butadiene, reported by Kotake and coll.[12] leads to exclusive formation of the 1,4-cyclohexenes. Heating compound 3bEE with methylvinylketone in toluene at 135°C for 72h yielded 48 % of adducts 6. The major product was purified by tlc and its structure was determined by ^1H NMR using double irradiation techniques in the presence of a shift reagent[13].

2-Benzenesulfonyl-1,4-dienes

We next investigated the preparation of 2-benzenesulfonyl-1,4-dienes by the method used for the synthesis of dienesulfones 3. Recently, Hsiao and Shechter[14] prepared compound 9a R=R^1=H from a silylsulfone precursor. Condensation of readily available lithiated E homoallylic sulfone 7 with heptanal followed by acetylation [8] of hydroxysulfones 8 R^1=H and elimination of acetic acid (2eq, NaOH, ether, r.t., 15h) yielded 44 % of dienesulfone 9b. ^1H NMR and hplc indicated that the

TABLE 2 : β-Elimination of β-functionalized sulfones 2



2 3 4 5

Entry	1 %Z[a]	2[b]	Base (eq.)	Solvents	Time h.	Yield %	3[c] 3EE	3EZ	3ZE	Minor Products Yield %
1	2	2a,R¹=Ac	NaOH (2)	dioxane	4	3a 67	90[d]			
2	2	2a,R¹=Ac	NaOH (4)	dioxane	62	3a 16[e]	100			4a 19 5a 16
3	0.5	2b,R¹=Ac	NaOH (4)	dioxane	2.5	3b 68	90	10		1 13 4b 6
4	0.5	2b,R¹=Ac and R¹=H 75/25	NaOH (2)	dioxane	2	3b 61	93	7		1 18 4b 9
5	0.5	2b,R¹=Ac	NaOH (2)	ether	3	3b 75	94	6		
6	0.5	2b,R¹=Ac	NaOH (1)	ethanol	1	3b 79	76	24		4b 10
7	0.5	2b,R¹=Ac	NaOEt (5)	ethanol	1	3b 61	85	15		4b 31
8	0.5	2b,R¹=Ts	NaOH (1.2)	dioxane-H_2O 1/1	3	3b 78	12	88		
9	18	2b,R¹=Ac	NaOH (4)	dioxane	2.5	3b 39	87[g]	2[g]	11[h]	1 10 x[i] 34

[a] hplc ; [b] diastereoisomer ratio of 2 is ~55/45 threo/erythro except for entry 7 where 2 b R¹=Ts contains only the threo isomer ; [c] ^1H NMR at 90 MHz ± 5 % ; [d] ^1H NMR at 80 MHz ; [e] 50/50 mixture of sulfones 3 and 5 ; [f] 2b R¹=Ac prepared as in Table 1, entry 4 ; [g] capillary-VPC ; [h] ^1H NMR at 250 MHz ± 3% ; [i] unidentified sulfones

product contained 96 % of 9bEE and 4 % of 9bEZ. Flash chromatography of the crude product afforded dienesulfone 9bEE > 99 % pure according to hplc (± 0.5 %). For analytical purposes a 63/32/5 mixture of 9b EE, 9b ZE and 9b EZ was prepared from a 61/39 mixture of 7E and 7Z (63 % overall yield). The 9b ZE isomer could be easily distinguished by ^1H NMR but compounds 9bEE and 9bZE were not separated by hplc.

As Z homoallylic sulfones are readily available[15] this method is also suitable for the synthesis of ZZ 1,4-dienes an important class of natural products [16]. The syntheses of 2-benzenesulfonyl-1,3- and 1,4- dienes, 3EE and 9EE, from E allylic and E homoallylic sulfones are highly stereoselective and by flash chromatography it is possible to obtain these compounds pure (> 99.5 % EE). The preliminary results obtained in the Diels-Alder reaction of 3bEE with methylvinyketone are encouraging. Better yields should be obtained with electron-rich dienophiles.In the following paper, the stereospecific reduction of dienesulfones 3 and 9 to 1,3- and 1,4-dienes is described.

Experimental Section

Elemental analyses ($C_nH_nS_n$ indicates C,H,S ± 0.3 %) were conducted at Paris VI, Centre de Spectrochimie. Analytical and preparative thin-layer chromatography (tlc) were performed on Merck PF 254 silica gel using eluent A (cyclohexane/dichloromethane/ethylacetate : 50/45/5) unless stated otherwise. A pentane /ether gradient was used for vacuum chromatography [17] (Merck 60H silica gel). Analytical hplc was conducted on a Du Pont 850 Liquid Chromatograph equipped with a Du Pont B 1500 Zorbax Sil. (4.6 mm x 25 cm) column.

Spectra were recorded on the following : Bruker WP-80, Varian EM 390 or Cameca 250 for ^1H NMR, Bruker WH-90 for ^{13}C NMR, Perkin-Elmer 599 for IR and Varian-Mat CH7 or Riber Nermag R10-10/B for m/z.

After workup all organic layers were dried over anhydrous magnesium sulfate. All solvents were distilled over appropriate reagents : benzophenone-sodium (THF,ether), P_2O_5 (pentane, cyclohexane, DMF), calcium hydride (CH_2Cl_2,$CHCl_3$). n-Butyllithium was titrated with a 1N solution of benzyl-

alcohol in toluene using 2,2'-biquinoline [18] as the indicator prior to use. All reactions were run under a positive pressure of dry nitrogen.

Synthesis of a 2-benzenesulfonyl-1,3-diene 3 Preparation of Compounds 2

A stirred solution of [(2-pentenyl)sulfonyl] benzene 1E (2.10 g, 10 mmol ; prepared according to ref. 6 > 99.5 % E) in 45 ml of THF was cooled to -78°C. 6.8 ml (1.05 equiv.) of n-butyllithium, 1.53 N in hexane (or the amount indicated in Table 1) were added dropwise, stirring was continued for 0.5 h and then the temperature was allowed to rise to -35°C. 2 h later 1.6 ml of heptanal (12 mmol) dissolved in 5 ml of THF were added. Stirring was maintained for 5 h between -35 and -30°C and 1.13 ml (12 mmol) of acetic anhydride (in situ acetylation, entries 1,2 Table 1)(or 12 mmol of tosylchloride for entry 5, Table 1) were added. The mixture was maintained at -30°C for an additional 15 h.

The reaction mixture was hydrolyzed with 1 ml of a saturated aqueous solution of ammonium chloride at -30°C. THF was evapored at reduced pressure, ether was added and the aqueous layer was extracted.

The combined organic layers were washed twice with an aqueous 10 % solution of sodium hydroxide (omitted for 2b R^1=Ts) followed by brine until neutral. The organic layer was dried, filtered and purified by vacuum chromatography [17] to furnish 3.17 g (90 % pure, 78 % yield) of 6-acetoxy-5-benzenesulfonyl 3-dodecenes 2b R^1=Ac (threo/erythro, 57/43). Spectral data for compounds 2 are collected in Table 3.

In the 2-step method we recommend, addition of aldehyde was followed by stirring at -35°C for 20 h. Hydrolysis (-35°C) and workup were performed as above (omitting washing with NaOH). Acetylation of 2b R^1=H was conducted as follows. 1.045 g (2.5 mmol) of hydroxysulfones 2b R^1=H (78 % pure), 0.5 ml (5mmol) of acetic anhydride, 0.75 ml (5 mmol) of triethylamine and 10 mg of 4-dimethylaminopyridine [8] were stirred at room temperature for 4 h. Workup and purification were

TABLE 3 : Spectral Data of Condensation Products 2

Compound	IR	m/z	^{1}H NMR (250MHz) in $CDCl_3$: δ = 0 ppm for TMS, J in Hz
threo, 2aEE[a] R=Et, R^1=Ac	1735,1300 1225,1140	311,251,169, 143,141,127,	0.89 (q,6H,7.8), 1.62 (m,2H), 1.86 to 2.18 (m,2H), 2.00 (s,3H), 3.90 (dd,1H, J_1=10.4,J_2=6.8), 5.24 to 5.6 (m,3H), 7.52 to 7.74 (m,3H), 7.86 to 7.92 (m,2H)
erythro, 2aEE R=Et,R^1=Ac		125	0.86 (t,3H,7.5), 0.94 (t,3H,7.5), 1.4 to 1.59 (m,1H), 1.59 to 1.78 (m,1H), 1.98 (s,3H), 1.98 to 2.2 (m,2H), 3.59 (brdd,1H,J_1~8,J_2~2), 5.46 to 5.7 (m,3H), 7.54 to 7.75 (m,3H), 7.84 to 7.92 (m,2H)
2bEE,R=n-Hex R^1=Ac	1740,1660, 1300,1230, 1150,1025, 970	367,307,225, 143,125,113	0.84 to 0.98 (m,6H), 1.17 to 1.38 (m,8H), 1.38 to 1.94 (m,2H), 1.94 to 2.16 (m, 5H containing two singlets at 1.98 and 2.00~3H), 3.55 (cdd,~0.55H,J_1=9,J_2=2), 3.9 (dd,~0.45H,J_1=10,J_2=6.2), 5.29 to 5.7 (m,3H), 7.54 to 7.73 (m,3H), 7.84 to 7.96 (m,2H)
2bEE,R=n-Hex R^1=Ts	1375,1310 1180,1150	378,364,337, 307,209,181 165,155,141 125,91	0.81 to 0.92 (m,6H), 1.02 to 1.32 (m,9H), 1.62 to 1.80 (m,1.5H), 1.88 to 2.08 (m,3H), 2.49 (s,3H), 4.08 (dd,1H,J_1=9.2,J_2=2.8), 5.04 (dt,1H,J_1=11.2,J_2~2.2), 5.34 to 5.5 (m,~H-ABXY$_2$-J_{AB}=15,J_{AX}=9.2,J_{BY}=6), 7.38 to 7.44 (d,2H,8), 7.56 to 7.64 (m,2H), 7.68 to 7.76 (m,1H), 7.78 to 7.88 (m,4H)
2bEE,R=n-Hex R^1=H	3500,1300, 1150,1085	325,307,183, 143,125	0.8 to 0.96 (m,6H), 1.2 to 1.66 (m,10H), 1.9 to 2.07 (m,2H), 2.10 (brd,0.6H,~2.2), 3.45 (dd,0.6H,J_1=10,J_2=1), 3.6 (dd,0.4H,J_1=10,J_2=9), 4 (brd, 0.4H,2.8), 4.33 (m,0.4H), 4.54 (m,0.6H), 5.19 (ddt,0.4H,J_1=15.5,J_2=10,J_3=1.3), 5.31 to 5.49 (2xdt,1H,J_1=15.5,J_2=6.3), 5.67 (ddt,0.6H,J_1=15.5,J_2=10,J_3=1.5),7.56 to 7.66 (m,2H), 7.66 to 7.76 (m,1H), 7.85 to 7.93 (m,2H)
2bEE+EZ R=n-Hex R^1=Ac			0.77 to 1.10 (m,~8H), 1.13 to 2.53 (m~16H containing 4 singlets at 2.00ppm) 3.53 to 3.67 (m,~0.5H), 3.78 to 4.01 (m,0.5H), 4.01 to 4.55 (br signals,~0.4H) 5 to 6 (m,3H), 7.43 to 8 (m,5H)

[a] $C_{16}H_{22}O_4S$

accomplished as above to yield 0.915 g, 77 % (78 % pure) of 2b R^1=Ac (threo/erythro : 56/44).

Preparation of 2-benzenesulfonyl-1,3-dienes 3 from compounds 2

0.469 g (1 mmol) of acetoxysulfones 2b R^1=Ac (78 % pure) obtained in two steps, 40 mg of freshly-ground sodium hydroxide, 5 ml of ether and 24 ul of water were stirred at room temperature for 3 h. The suspension was diluted with ether, washed with brine and dried. The solvent was evaporated to yield an oil (0.230 g, 75 %) which contained a 94/6 mixture of 3bEE and 3bEZ according to hplc analysis (decreasing R_f-eluent : ethylacetate/2,2,4-trimethylpentane : 3/97-precision ± 0.5 %). The percentage of isomer 3bZE was determined by ^{1}H NMR at 250 MHz (precision ± 2 %) as 3bEE and 3bZE were not separated by hplc. 3bEE and 3bEZ were separated on a preparative scale by FTash Chromatography [19] (9 cm x 15 cm column, eluent-ethyl-acetate/pentane : 6/94) to give each isomer > 99.5 % pure.

Both β-eliminations (Table 2) and base-catalyzed equilibrations of dienesulfones 3 were conducted as described above using appropriate reactions, parameters, base and solvent. For entries 6 and 7, Table 2, 1ml of water was added at the end of the reaction, the solvent was evaporated at reduced pressure and the residue diluted with ether followed by the usual workup. Compounds 4b were purified by preparative tlc (eluent A ; R_f3 > R_f4). Regioisomers 3 and 5 could not be separated but in the case of 3a and 5a the ratio of isomers could be determined with fair accuracy (± 5 % compared to ~10 % for 3b and 5b) by ^{1}H NMR. The spectral data for dienic sulfones 3, 4 and 5 are collected in Table 4.

Diels-Alder reaction of 3b EE with methylvinylketone

306 mg (1 mmol) of sulfone 3bEE, 0.8 ml of methylvinylketone (10 mmol), 5 ml of xylene and a few crystals of hydroquinone were heated at 135°C in a sealed tube for 3 days. The solvent was evaporated and the residue purified first by vacuum chromatography [17] and then preparative tlc (eluent : cyclohexane/dichloromethane/ethylacetate : 80/20/5-3 elutions). The first fraction

TABLE 4 : Spectral Data of dienic sulfones 3, 4 and 5

Compound	IR	m/z	^{1}H NMR (250 MHz) in $CDCl_3$: δ = 0 ppm for TMS, J in Hz
3aEE,R=Et[c]	1310,1155, 1145,970	250,143,125	0.93 (t,3H,7.5), 1.11 (t,3H,7.5), 2.08 (m,2H), 2.32 (quintuplet,2H,7.5), 5.88 to 6.08 (m,2H,J_{AB}=16.5,J_{BX}=5.5), 6.97 (t,1H,7.5), 7.5 to 7.67 (m,3H), 7.84 to 7.92 (m,2H)
3a,R=Et	1310,1150 970	250,143,125, 109	0.91 (t,3H,7.5), 1.73 (d,3H,5.5), 2.03 (m,2H), 4.14 (t,1H,7.5), 5.45 to 5.74 (m,4H), 7.52 to 7.71 (m,3H), 7.82 to 7.92 (m,2H)
3aEE+ 5aEE R=Et	1310,1155, 1145,970	250,143,125	0.95[t-q,3H,7.5 (t at 0.93 and t at 0.96)], 1.11 (t,1.5H,7.5), 1.54 (sextuplet, 1H,7.5), 1.75 (d,1.5H,5), 2.09 (m,1H), 2.3 (m,2H), 5.88 to 6.10 (m,2H), 6.95 (t,0.5H,7.5), 6.97 (t,0.5H,7.5), 7.5 to 7.68 (m,3H), 7.85 to 7.92 (m,2H)
3bEE,R=n-Hex[d]	1310,1150, 970	306,181,165, 143,125	0.84 to 0.97 (m,6H), 1.19 to 1.4 (m,6H), 1.4 to 1.56 (m,2H), 2.07 (m,2H), 2.29 (q,2H,7.5), 5.87 to 6.07 (ABX_2,2H,J_{AB}=16.5,J_{BX}=5.5), 6.97 (t,1H,7.5), 7.49 to 7.66 (m,3H), 7.83 to 7.9 (m,2H)
3bEE+ 3bZE (64/36)R=nHex			0.53 (t,1H,7.5), 0.8 to 1.0 (m,5H), 1.2 to 1.6 (m,8.7H), 2.06 (m,2H), 2.27 (q,1.3H,7.5), 5.66 to 6.05 (m,2H containing at high field AB,0.7H,J=11.2 and at low field A'B',1.3H,$J_{A'B'}$=16.5), 7.47 to 7.66 (m,3H), 7.82 to 7.90 (m,2H)
3bEZ,R=n-Hex		306,249,181, 165,143,125	0.78 to 1.12 (m,6H), 1.12 to 1.77 (m,8H), 2.10 (quintuplet,2H,7), 2.67 (q,2H, 7.5), 5.89 (dt,1H,J_{AB}=15.5,J_{AX2}=7), 6.17 to 6.31 (m,2H), 7.51 to 7.69 (m,3H), 7.85 to 7.95 (m,2H)
4b	1305,1145, 970	306,165,143, 141,125	0.84 to 0.98 (m,6H), 1.16 to 1.36 (m,6H), 1.99 to 2.13 (m,4H), 4.15 (t,1H,7.5), 5.46 to 5.71 (m,4H), 7.52 to 7.70 (m,3H), 7.81 to 7.90 (m,2H)

[a] UV(cyclohexane) λ max=224 nm (ε =17000) and for hplc analysis λ=265 (ε =2900) ; [b] UV (cyclohexane) λ max=222 nm (ε =18000) and for hplc analysis λ=265 (ε =62000) ;
[c] $C_{14}H_{18}O_2S$; [d] $C_{18}H_{26}O_2S$

(54 mg, 14 %) was composed of a 40/60 mixture of 2 isomeres 6A and 6B The second fraction (lower R_f)(126 mg,34 %) contained a single isomer 6C according to ^1H NMR at 250 MHz in the presence of $Eu(fod)_3$, F. 108°C(EtOH).

6A + 6B : m/z 376,333,306,235. ^1H NMR 0.8 to 2.12 (m, 20H), 2.17 (s,1.2H), 2.22 (s,1.2H), 2.22 (s,1.8H), 2.32 to 3.08 (m,3H), 7.09 (m,1H), 7.54 to 7.72 (m,3H), 7.88 to 7.97 (m,2H)
6C : IR 1700, 1300, 1150. m/z 376,333,306, 235. ^1H NMR 0.85 (t,3H,6.7), 0.97 (t,3H,7.5), 1.05 to 1.4 (m, 12H), 1.54 (br td, H_5,J_{5-6} ~13, J_{5-4}~11, J_{6-7}=5.5), 1.8 (br d, H_6,J_{6-5} ~13), 2.2 (s,3H), 2.4 (m,H_7), 2.7 to 2.9 (m, H_3 and H_4 ; at high field coupling with H_2 ; at low field and after adding Eu (Fod)$_3$-J_{4-3}~4-5, J_{4-5}~11 and J_{4-6}~2-3). Data was recorded in the presence of $Eu(FOD)_3$-d_{27} (Merck-Uvasol) 7 22(d,H_2, J = 4.5), 7.54 to 7.7 (m,3H),7.88 to 7.95 (m,2H).

Synthesis of [(2-butene-1-yl 1-octenyl) sulfonyl]benzene 9b EE
Hydroxysulfones 8 R^1=H

Compounds 8, R^1=H, were prepared by condensation of the lithio derivative of 7E[15c] (1.05 g, 5 mmol) of 7E ; 3.3 ml of 1.59N n-BuLi in hexane ; 50 ml of THF ; -78°C) with 0.8 ml (6 mmol) of heptanal at -35°C (15 h) followed by hydrolysis at -30°C with 1 ml of a saturated aqueous solution of ammonium chloride. Workup as described for 2 R^1=H and purification by vacuum chromatography led to 1.67 g (78 % chemical purity, 80 % yield) of 8, R^1=H.

Acetoxysulfones 8 R^1=Ac

1.56 g (3.7 mmol) of 8 R^1=H (78% pure), 1.5 ml(10 mmol) of triethylamine, 1 ml (10 mmol) of acetic anhydride and 50 mg of DMAP[8] were mixed at 0°C and then stirred at room temperature for 4 h. Workup and purification as previously described yielded 1.36 g (82 % chemical purity, 85 % yield) of 8 R^1=Ac.

[(2-Butene-1-yl-1-octenyl) sulfonyl] benzene 9b EE

0.716 g (1.6 mmol) of 8 R^1=Ac, 10 ml of dioxane and 0.160 g (2.5 equiv.) of freshly-ground sodium hydroxide pellets were stirred at room temperature for 15 h. Workup and purification by

TABLE 5 : Spectral Data of homoallylic compounds 7 and 8, and dienesulfones 9

Compound	IR	m/z	^1H NMR (250MHz) in $CDCl_3$: δ= 0 ppm for TMS, J in Hz
7E[a]	1310,1150, 975	211,143,125	1.52 (dd,3H,J_1=6.2,J_2=1.2), 2.32 (m,2H), 3.07 (m,2H), 5.18 to 5.33 (m,1H, J_{AB}=15), 5.37 to 5.52 (m,1H,J_{AB}=15), 7.5 to 7.71 (m,3H), 7.83 to 7.98 (m,2H)
8E,R^1=H	3510,1300, 1140,965	325,307,239, 182,165,143, 125,108	0.71 to 1.91 (m,~23H), 1.97 to 2.73 (m,2H), 2.98 to 3.38 (m,2H), 3.98 to 4.36 (m,1H), 4.90 to 5.82 (m,2H), 7.49 to 8.13 (m,5H)
8E,R^1=Ac	1735,1300, 1230,1140, 970	367,307,224, 143,125	0.68 to 3.58 (m,27H containing 2 singlets at 1.77 and 1.84 ppm 40/60), 4.90 to 5.80 (m,3H), 7.49 to 8.07 (m,5H)
8E+Z,R^1=Ac	1735,1300, 1230,1140, 970,690	367,307,224, 143,125	0.82 to 0.94 (m,3H), 1.14 to 1.4 (m,10H), 1.51 to 1.68 (m,3H), 1.83-1.85-1.91-1.93 (4 singlets,~3H-the first two in the ratio 70/30 represent ~27%, the second two singlets also present a 70/30 ratio), 2.34 to 2.86 (m,2H), 3.21 (m, 0.3H), 3.40 (m,0.7H), 5.17 to 5.63 (m,3H), 7.58 to 7.76 (m,3H), 7.9 to 8.01 (m,2H)
9bEE[b]	1300,1150, 965	307,181,143, 125	0.89 (t,3H,6.6), 1.24 to 1.39 (m,6H), 1.39 to 1.57 (m,5H containing a dd J_1=6.2,J_2=1.5 at 1.46ppm), 2.22 (m,2H,7.5), 2.98 (brd,2H,6.2), 5.02 to 5.16 (m,1H,J_{AB}=15.5), 5.22 to 5.38 (m,1H,J_{AB}=15.5), 7.03 (t,1H,7.5), 7.5 to 7.67 (m,3H), 7.86 to 7.93 (m,2H)
9bEE+9bZE[c]	1300,1145, 970,695	306,181,143, 125,84	0.89 (t,3H,6.8), 1.23 to 1.41 (m,6H), 1.41 to 1.67 (m, 5H containing 2 dd,J_1=7 J_2=1.5 at 1.46 and 1.56 ppm in a 2/1 ratio), 2.21 (q,2H,7.5), 3.00 (d,1.4H,6), 3.04 (d,0.6H,7), 4.93 to 5.17 (m,1H), 5.23 to 5.42 (m,1H), 6.07 (t,~0.05H, 7.5)[c], 7.15 (t,1H,7.5), 7.51 to 7.75 (m,3H), 7.87 to 8.05 (m,2H)

[a] $C_{11}H_{14}O_2S$; [b] $C_{18}H_{26}O_2S$; [c] also ~5% of 9b EZ ; [d] 90 MHz

Flash Chromatography led to 230 mg (33.5 %) of 9b as a 93/7 mixture of EE and EZ isomers and a second fraction of pure 9bEE (230 mg, 33.5 %) according to ^{1}H NMR analysis. The preparation of a 30/65/5 mixture of 9b ZE, 9b EE and 9b EZ from a 31/69 mixture of homoallylic sulfones 7 Z and 7 E was conducted in a similar manner. HPTc separated the EZ isomer (5 %) from the other 2 compounds 9b (eluent : 2,2,4-trimethylpentane/ethylacetate, 97/3 ; decreasing R_f).

Table 6 : Elemental Analysis

Compound	Molecular Formulae	Calculated % C	H	S	Observed % C	H	S
2aEE	$C_{16}H_{22}O_4S$	61.94	7.10	10.32	61.75	6.89	10.35
3aEE	$C_{14}H_{18}O_2S$	67.20	7.20	12.80	67.36	7.12	12.69
3bEE	$C_{18}H_{26}O_2S$	70.59	8.50	10.46	70.44	8.77	10.20
6C	$C_{22}H_{32}O_3S$	70.21	8.51	8.51	70.01	8.69	8.40
7E	$C_{11}H_{14}O_2S$	62.86	6.67	15.24	62.68	6.82	15.12
9bEE	$C_{18}H_{26}O_2S$	70.59	8.50	10.46	70.73	8.58	10.27

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