Tetrahedron Vol. 42, No. 19, pp. 5321 to 5328, 1986
Printed in Great Britain.

0040-4020/86 $5.00+.00

SYNTHESES WITH SULFONES XLV : STEREOSELECTIVE PREPARATION OF 1- BENZENESULFONYL-1,3-DIENES

T. CUVIGNY, C. HERVE du PENHOAT, and M. JULIA*

ECOLE NORMALE SUPERIEURE, Laboratoire de Chimie,
24, rue Lhomond, 75231 PARIS CEDEX 05 - FRANCE

(*Received in France* 28 *July* 1986)

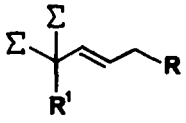
Abstract : The stereoselective preparation of EE 1-benzenesulfonyl-1,3-dienes is described. Michael addition and Diels-Alder cycloaddition of these compounds are reported.

In connection with a study of allylic 1,1-disulfones, [1,2] we investigated basic elimination of a sulfonyl moiety from these compounds to furnish 1,3-dienes functionalized by the benzenesulfonyl group. Our preliminary results showed that this reaction is regiospecific[3]. A new preparation of Z olefins,[4,5,6] recently described, is based on the stereospecific reduction of the sulfonyl moiety of E vinylsulfones with sodium dithionite[5] or with Grignard reagents under transition -metal catalysis[6]. Full details of the stereoselective preparation of 1-benzenesulfonyl-1,3-dienes are given here as well as some aspects of their reactivity. In the next paper[7] the preparation of 2-benzenesulfonyl-1,3- and -1,4- dienes is described and in the third one[8] the stereospecific reduction of the sulfonyl group of these 1,3- and 1,4- dienes is reported.

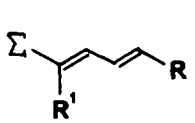
The methods recommended for the synthesis of 1,3-dienes functionalized by the sulfonyl group were not satisfactory for our purposes. Either the starting materials were not readily available [9a-h] or the stereoselectivity of the method had not been studied [9i-j]. The first technique we investigated was basic elimination of benzenesulfinic acid from readily available allylic 1,1-disulfones[1]. Although elimination from allylic substrates is known to be regioselective, this reaction is generally not stereoselective [10]. However in the related S_N2' type reaction of allylic 1,1-disulfones, formation of γ-functionalized E vinylsulfones was highly stereoselective[2]. In the present case, the E configuration for the double-bond bearing the sulfonyl group and an E/Z mixture for the other double bond could be anticipated.

Various conditions recommended for eliminating benzenesulfinic acid [11] were tried. Best results were obtained upon heating the allylic disulfones with 2 equivalents of powdered sodium hydroxide in a 1/1 mixture of t-BuOH and toluene (benzene) in the presence of molecular sieves, Table 1. In the case of 1 the product contained 65 % of a single isomer identified by ^{1}H NMR as 2 as well as 23 % of starting disulfone 1, entry 1. Prolonged reaction led to polymer formation, entry 2. Two isomers were obtained from 3, entry 4, in 77 % total yield along with 23 % of unchanged starting material. Structures 4 EE and 4 EZ were attributed by ^{1}H NMR and the isomer ratio, 72/28 EE/EZ, was confirmed by hplc. In the case of 5, entry 5, heating at 105°C for 1h furnished 17 % of a 5/10/2 mixture of three dienesulfones which were separated by preparative hplc and identified by ^{1}H NMR as compounds 6 EE, 6 EZ and 7 respectively. It might be preferable to accept incomplete conversion since isomerisation to the more stable[12] allylic 2,4-diene sulfones increases with longer reaction times, entries 5 and 6. Equilibration of the EE/EZ mixtures of both

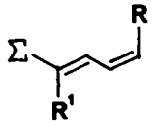
FORMULAE



1 R=H, R^1=Me
3 R=R^1=Me
5 R=n-Bu, R^1=Me

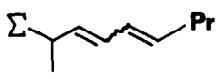


EE

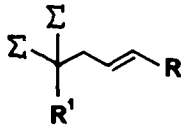


E Z

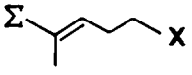
2 R=H, R^1=Me
4 R=R^1=Me
6 R=n-Bu, R^1=Me
17 R=Me, R^1=H
18 R=R^1=H



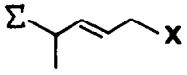
7



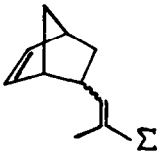
8 R=R^1=Me



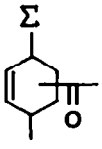
11 X=-N⬡
12 X= Σ
13 X=OEt



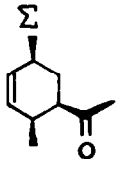
9 X=PhS
10 X=CH(CO Me) COOEt
14 X=-N⬡
15 X= Σ **16** X=OEt



19



20



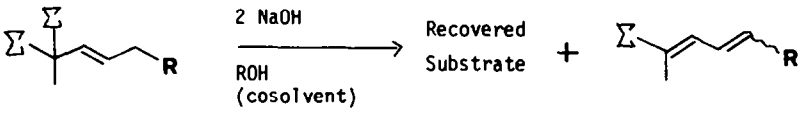
20C

4 and 6 with iodine as described by de Waard and coll. [9d] led to mixtures containing 85 % of the EE isomer and only 15 % of the EZ derivative.

As higher olefinic purity was required we next investigated 1,2-elimination of benzenesulfinic acid from readily available pure E homoallylic 1,1-disulfones [13], Table 2. The most satisfactory results, 38 % of 4, were obtained by stirring a heterogeneous mixture of 1,1-disulfone 8 in toluene with two equivalents of t-BuOK for 15 minutes at room temperature, entry 5. Longer reaction times did not increase the yield of 4 probably due to anionic polymerisation [14] of the product, entry 6. This time the EE/EZ isomer ratio determined by hplc and ^{1}H NMR was 98.5/1.5. Since our preliminary report Backvall and coll.[14] have described a stereoselective synthesis of 1,3-dienesulfones from 1,3-dienes.

TABLE 1 : 1,4-Elimination of benzenesulfinic acid from allylic 1,1-disulfones 1 with sodium hydroxide

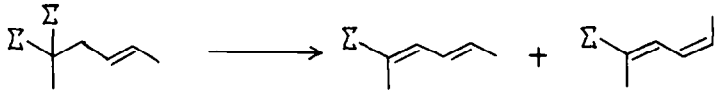
1 R = H
3 R = Me
5 R = nBu



Entry	Substrate	Temp °C	Time[a] h.	Recovered Substrate Yield	[b]1,3-Dienesulfone Yield %	Isomer Ratio[c] EE %	EZ %	Other products[b] %
1	1	80	8	23	2 65			
2	1	80	15	27	2 41			d
3	3	100	1	63	4 36	87	13	
4	3	100	4	23	4 77	72	28	
5	5	105	1	78	6 15	32	68	7 2
6	5	105	7	17	6 31	41	59	7 36

[a] cosolvent-benzene (entries 1-2) or toluene (entries 3-6) ; 0.3 g of molecular sieves (3 A°) per mmol of substrate ; [b] purified product ; [c] ^1H NMR ; [d] polymers

TABLE 2 : 1,2-Elimination of benzenesulfinic acid from homoallylic 1,1-disulfone 8



8 4 E E 4 E Z

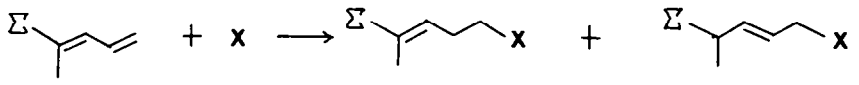
Entry	Base (equiv.)	Solvent	Conditions Temp °C	Time h	Yield %	4[a] Isomer Ratio EE	EZ	8 Yield %
1	DBU (1)[b]	CH_2Cl_2	20	48				88
2	TritonB(1)[c]	MeOH	65	48				82
3	TritonB(1)	Toluene/ tBuOH (1/1)	100	0.75	90	76	24	
4	NaOH (2)	Toluene/ tBuOH (1/1)	97	0.25	32	82	18	63
5	t-BuOK (2)[d]	Toluene	25	0.25	38	98.5	1.5	28
6	t-BuOK (2)	" "	25	0.5	21	99	1	29

[a] hplc and ^1H NMR ; [b] see ref. 11 i ; [c] see ref. 11 f ; [d] see ref. 13

Michael addition to 1-arene (or alkane) sulfonyl 1,3-butadienes has been studied [15]. 1-Sulfonyl 2-methyl 1,3-butadienes undergo regio and stereoselective 1,4-addition with various nucleophiles to give the E olefin [9f]. The results obtained by the addition of various nucleophiles to sulfone 2 are collected in Table 3. In the case of soft nucleophiles such as sodium thiophenoxide, entry 1, or sodio ethylacetoacetate, entry 2, the expected 9E and 10E 1,4-adducts were formed in 100 % and 62 % yields respectively. However harder nucleophiles such as piperidine, entry 3, sodium sulfinate, entry 4, and sodium ethoxide, entry 5, led to mixtures of isomers which were separated by preparative hplc and tlc in the latter two cases and identified as 3,4-adducts

(11, 12 and 13) and 1,4-products (14, 15 and 16) by ^{1}H NMR. In the run with sodium ethoxide, entry 5, 31 % of unchanged 2 was also recovered. It is noteworthy that the least stable regioisomer is the major product in this reaction. Dienesulfone 2 polymerises under basic conditions which would explain the moderate overall yields observed in certain runs. When dienic sulfone 2 was treated with 5 equivalents of sodium sulfinate in boiling ethanol [16,15b,9g] a 72/14/13 mixture of products was obtained in 96% yield. After separation by preparative hplc the products were identified by ^{1}H NMR as the 17EE, 17EZ and 2 isomers. This same product ratio was obtained when a 93/6/1 mixture of sulfones 17EE, 17EZ and 2 were treated in a similar way. This equilibration reaction, first described by Julia and Lavé [9g] is thought to proceed by an addition-elimination mechanism.

TABLE 3 : Michael addition of various nucleophiles to dienic sulfone 2



2

Entry	Nu (eq.)	Solvent and/or catalyst	Temp °C	Time h	5 Yield %	6 Yield %
1	PhSH (1)	EtOH + Na (0.5)	25	3		9 100
2	$CH_2(COCH_3)(COOEt)$ (1)	EtOH + Na (1)	80	7		10 62
3	piperidine	MeOH	65	3	11[a] 12	14[b] 70
4	ΣNa (5)	DMF, $HNEt_3Br$ (1.2)	100	24	12[b] 26	15[b] 39
5	EtONa	EtOH + NaOH (10)	25	22	13[c] 31	16[c] 9

a) isomer ratio determined by ^{1}H NMR ; b) separated by preparative hplc ; c) separated by preparative tlc ; also 31 % of 2

[2+2] π cycloaddition of 18 R=R^1=H with ynamines has been described by Eisch [9j] but to our knowledge only one case of [4+2] π cyloaddition of 1-sulfonyl-1,3-dienes with dienophiles has been reported[17]. However, benzenesulfonylcyclohexenes have been prepared from various 1,3-dienes using benzenesulfonylethylene as the dienophile [18]. Heating diene sulfone 2 in toluene (0.5M) with cyclopentadiene at 110° for 38 hours led to 55 % of a 55/45 mixture of products which were separated by tlc. By comparison of their ^{1}H NMR spectra with those of related compounds [19] it was possible to attribute the 19 exo and 19 endo structures to the major and minor components. Under similar conditions (xylene, 150°, 5d) but this time with 2 as the diene and methylvinylketone as the dienophile, no cycloaddition products were obtained. However, heating a 59/11/30 mixture of 17 EE, 17 EZ and 2, 0.5M in toluene with methylvinylketone for 96 h yielded 49 % of adducts 20A, 20B and 20C, and 38 % of starting 17. The major cycloaddition product, 20C obtained pure by tlc in 42 % yield with respect to transformed 17, was identified by ^{1}H NMR as the endo isomer. Considering that starting 17 contained 16 % of the EZ isomer the stereoselectivity of the reaction, 66 %, is fair. M.O. theory predicts low selectivity for dienes with electron-attracting substituents in the 1 position [20].

In conclusion, 1-benzenesulfonyl-1,3 dienes have been prepared as a 85/15 mixture of EE and EZ isomers from allylic 1,1-disulfones or pure (>98 % EE) from homoallylic 1,1-disulfones in mediocre yield. Reaction of these compounds with nucleophiles leads to 1,4-adducts in the case of soft nucleophiles and mixtures of 3,4- and 1,4 adducts in the case of hard ones. 1,3-Dienesulfones react both as dienophiles and as dienes in [4+2] π cycloaddition reactions. In the latter reaction, better yields should be obtained with electron-rich dienophiles.

Experimental Section

Elemental analyses ($C_nH_mS_p$ 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 [21] (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 benzylic alcohol in toluene using 2,2'-biquinoline [22] as the indicator prior to use. All reactions were run under a positive pressure of dry nitrogen.

Preparation of Allylic 1,1-Disulfones

Primary allylic 1,1-disulfones, were obtained by condensation of bisphenylsulfonylmethane with the appropriate aldehyde in the presence of piperidine acetate and molecular sieves [1]. Substituted compounds were prepared by metallation of the primary allylic 1,1-disulfones (NaH,DMF) followed by reaction with alkyliodides [1].

Preparation of 1-benzenesulfonyl-1,3-dienes by 1,4-elimination of benzenesulfinic acid from allylic 1,1-dissulfones

0.40 g (2 equiv.) of freshly-ground NaOH were added portionwise at regular intervals over a 5h period to a stirred suspension of disulfone 1 (1.75 g, 5mmol) and molecular sieves (0.5 g ; 3 A°) in a mixture of tertiobutanol (25ml) and benzene (or toluene ; 25 ml) at 80°C. A gradual precipitation of sodium benzenesulfinate was observed.
After heating a total of 7h the mixture was cooled, diluted with dichloromethane, filtered over Celite washed with water until neutral and dried. After evaporation of the solvents in vacuo the residual oil was purified by vacuum chromatography [21] (pentane-ether) to yield 0.68 g (65%) of (1-methyl 1,3-butadienyl) sulfonyl benzene, 2E and 0.4g of 1(23%).

Spectral data for 1-benzenesulfonyl-1,3-dienes are collected in Table 4. These compounds should be stored in dilute solutions at low temperature (-40°C). The other 1-benzenesulfonyl-1,3-dienes were prepared in a similar way according to the parameters indicated in Table 1.

Equilibration of 1-benzenesulfonyl-1,3-dienes with Iodine [9d]

50 mg (0.19 mmol) of an 88/12 mixture of 6 (EE/EZ : 32/68) and 7, 24 mg of iodine (0.5 equiv.) and 8 ml of ether were stirred at room temperature for 0.5h. The mixture was washed twice with a saturated solution of aqueous sodium thiosulfate followed by brine. Workup was completed as above to furnish 47 mg (94%) of an 86/14 mixture of 6 (EE/EZ,85/15) and 7 according to ^1H NMR (250 MHz) and hplc analysis. All iodine-catalysed equilibrations were conducted in a similar manner.

Michael Additions to (1-methyl 1,3-butadienyl) sulfonyl benzene 2E

10 ml of a 0.05 M solution of 2E in dichloromethane were evaporated just prior to use followed by addition of 0.5 ml of benzene for all reactions of dienic sulfones.

(1-Methyl 4-phenylthio 2-butenyl) sulfonyl benzene 9, X=SPh.

An ethanolic solution of sodium thiophenoxide (2.7 equiv. ; 0.15 ml of benzenethiol, 2ml of a 0.125 N sodium ethoxide in ethanol) was syphoned under nitrogen pressure into a stirred solution of 2E in a mixture of 3 ml of ethanol and 0.5 ml of benzene. Stirring was continued for 3h at room temperature, the solution was diluted with ether and washed twice with aqueous 5% NaOH followed by water. The organic layer was dried, filtered and the solvents were evaporated. The residual oil was purified by preparative tlc (eluent A) to yield 160 mg (100%) of 9 X=SPh F. 49.5-50°C.

Spectral data for addition products are collected in Table 5.

2-Acetyl 6-benzenesulfonyl-4-ethylheptenoate 10, X=CH($COCH_3$)CO_2Et

To a stirred solution of 0.125M sodium ethoxide in ethanol (4ml) were added 65mg (0.5mmol) of ethyl acetylacetonate followed by 0.5 mmol of diene 2E in a mixture of 1ml of ethanol and 0.5 ml of benzene. The mixture was heated at 80°C for 7h, diluted with ether, washed with water and treated as above to furnish 105mg (62%) of 10 X=CH($COCH_3$)CO_2Et.

4-Benzenesulfonyl-1-piperidino-2-pentene 14, X=-N⟨⟩ and
4-Benzenesulfonyl-1-piperidino-3-pentene 11, X=

5 mmol of compound 2E in 0.5 ml of benzene, 50 ul of piperidine and 3ml of ethanol were stirred at 65°C for 3h. Workup followed by preparative tlc yielded 120mg (82%) of a 15/85 mixture of 11 and 14 X=piperidinyl according to ^1H NMR analysis.

TABLE 4 : Spectral data of 1-benzenesulfonyl-1,3-dienes and 2,4-diene 7.

Compound	U.V.(MeOH)	m/z	^{1}H NMR(250MHz) in $CDCl_3$: δ = 0 ppm for TMS, J in Hz
2[a] R=H,R^1=Me	249 (27000)	208,125	1.96 (brs,3H), 5.62 (brd,1H,10), 5.74 (brd,1H,16.5), 6.59 (ddd,1H,J_1=16.5,J_2=11 J_3=10), 7.31 (brd,1H,11), 7.5 to 7.7 (m,3H), 7.86 to 7.92 (m,2H)
4EE + 4EZ[b] R=R^1=Me		222,143 125	1.90 (2 brs:1/3:6H), 6.04 to 6.34 (m,2H), 7.33 (brd,0.7H,9) 7.52 to 7.72 (m,3.3H), 7.86 to 7.96 (m,2H)
6 EZ[c] R=n-Bu, R^1=Me	262 (18000) 222 (15000) 265[e](17000)	264,125	0.94 (t,3H,7), 1.3 to 1.6 (m,4H), 1.92 (brs,3H), 2.37 (q,2H,7), 5.95 to 6.1 (m,1H, J_{AB}=11.2), 6.1 to 6.36 (m,1H), 7.54 to 7.74 (m,4H), 7.9 to 7.98 (m,2H)
6 EE[c] " "	260 (24000) 221 (12000) 265[e](22000)	264,125	0.93 (t,3H,7), 1.2 to 1.5 (m,4H), 1.92 (brs,3H),2.25 (q,2H,6.7), 6.3 (m,2H, J_{AB}=15.8), 7.36 (brd,1H,10.3), 7.54 to 7.72 (m,3H), 7.9 to 7.99 (m,2H)
17EE R=Me R^1=H	256 (14000) 220 (br signal)	208,125	1.88 (d,3H,6.2), 6.14 (brdd,1H,J_1=15,J_2=10.5), 6.24 to 6.44 (m,2H,J_{AB}=15), 7.53 to 7.70 (m,3H), 7.91 to 7.99 (m,2H)
7[d]		264,125	0.88 (t,3H,7.5), 1.14 to 1.64 (m, 7H), 1.88 to 2.4 (m,2H,containing at 2.05-q, 1.4H,7), 3.58 to 3.92 (m,1H,containing at 3.75-t, 0.7H,7.5), 5.06 (m,0.25H), 5.4 to 5.91 (m,2H), 5.91 to 6.38 (m,2H), 7.4 to 7.78 (m,3H), 7.86 to 8.24(m,2H)

[a] $C_{11}H_{12}O_2S$; [b] $C_{12}H_{14}O_2S$; [c] separated by hplc (eluant : dichloromethane/ethylacetate : 90/10) t_R 6EZ < t_R 6EE : > 90 % isomeric purity, $C_{15}H_{20}O_2S$; [e] wavelength used for UV detection during hplc analysis (eluent : ethylacetate / 2,2,4-trimethylpentane : 5/95) ; [d] chemical purity~85 %.

TABLE 5 : Spectral Data of Michael Adducts

Compound	IR	m/z	^{1}H NMR (250MHz) in $CDCl_3$: δ = 0 ppm for TMS, J in Hz
9 X=SPh[a,d]	1300,1150	318,209,177, 149,141,135, 109	1.26 (d,3H,7), 3.41 (dd,2H,J_1=6,J_2=1,5), 3.59 (br quintuplet,1H,7), 5.46 to 5.72 (m,2H,J_{AB}=15), 7.18 to 7.44 (m,5H), 7.46 to 7.66 (m,3H), 7.7 to 7.76 (m,2H)
10 X=CH(CO_2Et)(COMe)[b,e]	1725,1702 1300,1150	338,298,197	1.28(t,3H,7), 1.41 (d,3H,7), 2.24 (s,3H), 2.56 (m,2H), 3.46 (t,1H,7.2), 3.7 (br quintuplet,1H,7), 4.26 (q,2H,7), 5.42 to 5.64 (m,2H), 7.54 to 8.04 (m,5H)
14 X=  [f]	1300,1150	293,152,98	1.32 to 1.66 (m,8.5H,contained at 1.47:d,2.5H,7), 1.84 (brs, 0.5H), 2.08 to 2.56 (m,4.5H), 2.8 to 3 (m, 2H), 6.96 (brt, 0.15H,6.6), 7.48 to 8 (m,5H)
11 X= "	972		
15 X=  [g]	1300,1150 980	350,209	1.33 (d,3H,7), 3.73 (quintuplet,1H,7), 3.80 (brd,2H,5.8), 5.51 to 5.69 (m,2H), 7.43 to 8.03 (m,10H)
12 "			1.85 (brs,3H), 2.68 (brq,2H,7.5), 3.30 (brt,2H,7.5), 6.83 (brt,1H,7.5), 7.5 to 8,1 (m,10H)
16 X=OEt[ch]		301,255,227, 209,199,186, 149,143,141, 131,125,113	0.9 to 1.89 (m,10.7H containing at 1.42:d,2.1H,7.5), 3.14 to 4.34 (m,6.5H), 5.33 to 5.87 (m,1.3H), 7.43 to 8.02 (m,5H)
13 "	1300,1260 1070	224,210,196, 169,161,143, 141,125	1.19 (t,3H,7), 1.86 (brs,3H), 2.48 (brq,2H,7), 3.54 (dq,4H,7), 6.98 (dq,1H, J_1=7.5,J_2=1), 7.5 to 8 (m,5H)

[a] ^{13}C NMR($CDCl_3$-75.6,77.0,78.4)13.6,26.2,35.6,36.0,63.2,125.8,126.3,128.2,128.6,128.9,130.0,132.7, 133.3,134.9,136.6 ; [b] ^{13}CNMR($CDCl_3$-75.6,77.0,78.4)13.3,13.6,14.2,29.0,29.3,29.8,30.8,58.7,61.5,63.3 125.6,127.8,128.6,128.9,132.9,133.3,133.6,136.7,168.3,201.3 ; [c] chemical purity~65 % [d] $C_{17}H_{18}O_2S$ [e] $C_{17}H_{22}O_5S$; [f] $C_{16}H_{23}O_2S$; [g] $C_{17}H_{18}O_4S_2$; [h] $C_{13}H_{18}O_3S$

1,1'-[(1-Methyl-2-butene-1,4-diyl)bissulfonyl] bisbenzene 15, X=Σ and
1,1'-[(1-Methyl-1-butene-1,4-diyl)bissulfonyl] bisbenzene 12, X=Σ

410 mg (2.5 mmol) of sodium benzenesulfinate, 110 mg (1.2 equiv.) of triethylamine bromhydrate, 0.5 mmol of sulfone 2E and 5 ml of DMF were stirred at 100°C for 24h according to Bordwell and collaborators' [9] procedure. Workup and preparative tlc led to 112 mg (64 %) of a 32/68 mixture of disulfones 12 and 15, X=Σ. Both isomers were obtained > 90 % pure by preparative hplc (eluent A). The major isomer 15 crystallized, F. 168-9°C.

1-Ethoxy-4-benzenesulfonyl-3-pentene 13, X=OEt and
1-Ethoxy-4-benzenesulfonyl-2-pentene 16, X=OEt

1 mmol of sulfone 2E, 0.5 ml of benzene and 5 ml of a 2M ethanolic solution of sodium hydroxide were stirred at room temperature for 22 h. Workup and preparative tlc led to 65 mg (31 %) of sulfone 2E, 79 mg (31 %) of 13, X=OEt and 28 mg of a mixture of 16, X=OEt (~9 %) and an unidentified sulfone.

Reaction of 1-benzenesulfonyl-1,3-dienes with sodium benzenesulfinate

1 mmol of sulfone 2 dissolved in 0.5 ml of benzene, 0.820 g (5 mmol) of sodium benzenesulfinate and 5 ml of ethanol were stirred at 80°C for 24 h. Workup furnished 0.200 g (96 %) of a 14/14/72 mixture of 3 sulfones according to hplc analysis (eluent : dichloromethane/hexane : 90/10 ; decreasing R_f)

The first compound was identified as being unchanged 2 and the major component obtained 93 % pure by preparative hplc (same eluent) was identified as 17EE by ^1H NMR analysis.

Diels-Alder Reactions of Sulfone 2 with cyclopentadiene

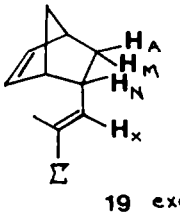
600 mg of cyclopentadiene (depolymerized according to ref.23) 1mmol of sulfone 2E dissolved in 2 ml of toluene and a few crystals of hydroquinone were heated in a sealed tube at 110°C for 38 h. Workup and preparative tlc (eluent : cyclohexane/ethylacetate : 90/10-7 elutions) yielded (decreasing R_f) 80 mg (29 %) of (2'-benzenesulfonyl)-1-propene-2-yl-bicyclo-[2.2.1]-5-heptene 19 exo and 70 mg (24 %) of (2'-benzenesulfonyl)-1-propene-2-yl-bicyclo [2.2.1]-5-heptene 19 endo, F.88-90°C.

Spectral data for Diels-Alder adducts are collected in Table 6.

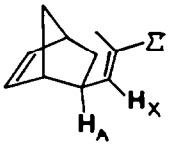
with methylvinylketone

1 mmol of a 59/11/30 mixture of sulfones 17EE, 17EZ and 2, 5 ml of toluene, 1 ml of methylvinylketone and a few crystals of hydroquinone were heated at 110°C in a sealed tube for 4 days. Workup and purification first by vacuum chromatography [21] followed by preparative tlc (eluent : cyclohexane/dichloromethane/ethylacetate : 70/30/5-4 elutions ; decreasing R_f) led to 102.4 mg (50 %) of sulfones 2 (47/53 : 2/17), 25 mg (13 %) of a 1/1 mixture of adducts 20A and 20B, 15 mg of 20B (δcharacteristic-0.79 and 2.06)(8 %) and 55 mg of (2-methyl-5-benzenesulfonyl) cyclohex-3ene methylketone 20C F.104-104.5°C (petroleum ether).

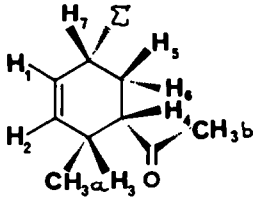
TABLE 6 : Spectral Data of Diels-Alder Adducts



19 exo



19 endo



20 C

Compound	IR	m/z	^1H NMR(250MHz) in $CDCl_3$: δ = 0 ppm for TMS, J in Hz
19 exo[18]	1300,1150	275,209	1.40 to 1.54 (m,4H), 1.84 (d,3H,1.2), 2.22 (m,1H,J_{AX}=9.5), 2.69 (brs,1H), 2.98 (brs,1H), 6.1 to 6.2 (m,2H), 6.91 (brd,1H,J_{AX}=9.5), 7.5 to 7.97 (m,5H)
19 endo[18]	1620,1290, 1145	275,209	0.88 (brd,H_A,J_{AM}=11.5), 1.31 (brd,1H,8.2), 1.49(brd,1H,8.2), 1.87 (brs, 3H), 2.05 (m,H_M,J_{AM}=11.5), 2.83 to 2.97 (m,3H,2.9 : H_N,J_{NX}=10), 6.07 (brdd,1H,J_1=5.5 J_2=3), 6.30 (brdd,1H,J_1=5.5,J_2=3), 6.51 (brd,H_X,J_{NX}=10), 7.51 to 7.93 (m,5H)
20A and 20B		209,143,141, 137,125	[c] 0.79 to 3.04 (m,10H containing at 0.79 (d,1.5H,7), at 0.94 (d,1.5H,7), at 2.06 (s,1.5H) and at 2.4 (s,1.5H) , 3.41 (m,0.5H), 4.4 (m,0.5H), 5.51 to 6.17 (m,2H), 7.61 to 8.14 (m,5H)
20C[b]	1735, 1295, 1130	279,221,207, 137	0.54 (d,CH_{3a},6.8), 1.74 (brq, H_6,~13-14 simplifies-J_{6-5}=14, J_{6-7}=12, J_{6-4}=14), 2.05 (brdd,H_5,J_{5-6}=14,J_{5-7}=6,J_{5-4}~2.5), 2.12 (s,CH_{3b}), 2.62 to 2.78 (m,H_4 and H_3), 3.89 (m,H_7,J_{7-6}=12,J_{7-5}=6), 5.91 (brd,H_1,J_{1-2}=11,J_{1-7}~1.5), 6.06 (m,H_2, J_{2-3}=5,J_{2-7}=2.5), 7.86 to 7.94 (m,2H)

[a] Elemental analysis (C,H,S ±0.3%) of exo/endo mixture $C_{16}H_{18}O_2S$; [b] unstable under elemental analysis conditions ; [c] ^1H NMR at 80MHz

Table 7 : Elemental Analysis

Compound	Molecular Formulae	Calculated % C	H	S	Observed % C	H	S
2	$C_{11}H_{12}O_2S$	63.46	5.77	15.38	63.53	5.94	15.40
4 EE + EZ	$C_{12}H_{14}O_2S$	64.86	6.31	14.41	64.83	6.33	14.21
6	$C_{15}H_{20}O_2S$	68.18	7.58	12.12	68.28	7.76	12.02
9 X = SPh	$C_{17}H_{18}O_2S$	64.15	5.66	20.13	64.23	5.75	19.85
10X = CH(COMe)CO$_2$Et	$C_{17}H_{22}O_5S$	60.35	6.51	9.46	60.18	6.70	9.37
11+14 X = N⟨ ⟩	$C_{16}H_{23}NO_2S$	65.53	7.85	10.92	65.58	7.93	10.83
12+15 X = Σ	$C_{17}H_{18}O_4S_2$	58.28	5.14	18.28	58.06	5.29	18.27
13X = OEt	$C_{13}H_{18}O_3S$	61.42	7.09	12.60	61.37	7.04	12.48
19endo + exo	$C_{16}H_{18}O_2S$	70.07	6.57	11.68	70.02	6.77	11.75

Financial help from the LA32 and A.T.P. "Messagers Chimiques" is gratefully acknowledged. We thank Miss Michon, Miss Derouet and Mrs Morin for recording NMR and glc-mass spectra.

References

1. T. Cuvigny, C. Hervé du Penhoat and M. Julia, Bull. Soc. Chim. France, II, 43 (1982) ; **2.** T. Cuvigny, C. Hervé du Penhoat and M. Julia, accepted at Rec. Trav. Chim. Pays Bas ; **3. a)** T. Cuvigny, C. Hervé du Penhoat and M. Julia, Tetrahedron Letters, 24, 4315 (1983) ; **b)** T. Cuvigny, J. L. Fabre, C. Hervé du Penhoat and M. Julia, Tetrahedron Letters, 24, 4319 (1983) ; **4.** M. Julia, M. Launay, J. P. Stacino and J. N. Verpeaux, Tetrahedron Letters, 23, 2465 (1982) ; **5.** J. Bremner, M. Julia, M. Launay and J. P. Stacino, Tetrahedron Letters, 23, 3265 (1982) ; **6.** J. L. Fabre and M. Julia, Tetrahedron Letters, 24, 4311 (1983) ; **7.** T. Cuvigny, C. Hervé du Penhoat and M. Julia, Tetrahedron following paper ; **8.** T. Cuvigny, C. Hervé du Penhoat and M. Julia Tetrahedron, paper after the following paper ; **9. a)** M. Asscher and D. Vofsi, J. Chem. Soc., 4962 (1964) ; **b)** W.E. Truce, C.T. Goralski, L. W. Christensen and R. H. Bavry, J. Org. Chem., 35, 4217 (1970) ; **c)** G. L. Olson, H. C. Cheung, K. D. Morgan, C. Neukom and G. Saucy, J. Org. Chem., 41, 3287 (1976) ; **d)** J. J. Burger, T.B.R.A. Chen, E.R. de Waard and H. O. Huisman, Tetrahedron, 36, 723 (1980) ; **e)** M. M. Tanaskov, M. D. Stadnichuk and L. V. Kekisheva, Zhurn. Obshchei Khim., 50, 1738 (1980); **f)** M. Julia, D. Lave, M. Mulhauser, M. Ramirez-Munoz and D. Uguen, Tetrahedron Letters, 24, 1783 (1983) ; **g)** D. Lave, Thèse de Docteur-Ingénieur, Paris VI, 1978 ; **h)** F. Naf, R. Decorzant and S. Esher, Tetrahedron Letters, 23, 5043 (1982) ; **i)** F. G. Bordwell and T. G. Mecca, J. Am. Chem. Soc., 94, 5829 (1972) ; **j)** J. J. Eisch, J.E. Galle and L.E. Hallenbeck J. Org. Chem., 47, 1608 (1982) ; **10. a)** K. H. Overton, Chemical Society Reviews, 8, 447 (1979) ; **b)** F. L. Greenwood and J. A. Sedlak, J. Org. Chem., 22, 776 (1957) ; **c)** S. J. Cristol, W. Barasch and C. H. Tieman, J. Am. Chem. Soc., 77, 583 (1955) ; **d)** A. Thibblin and P. Ahlberg, J. Am. Chem. Soc., 101, 7311 (1979) ; **e)** R. K. Hill and G. R. Newkome, J. Am. Chem. Soc., 91, 5893 (1969) ; **f)** D. K. Onderka and H. G. Floss, J. Am. Chem. Soc., 91, 5894 (1969) ; **g)** H. G. Floss, D. K. Onderka and M. Carroll, J. Biol. Chem., 247, 736 (1972) ; **h)** R. K. Hill and M. G. Bock, J. Am. Chem. Soc., 100, 637 (1978) ; **11. a)** R. A. Bartsch and J. F. Bunnett, J. Am. Chem. Soc., 91, 1376 and 1382 (1969) ; **b)** A. K. Colter and R. E. Miller, J. Org. Chem., 36, 1898 (1971) ; **c)** T. J. Wallace, A. Schriesheim and J. E. Hofmann, J. Am. Chem. Soc., 85, 2739 (1963) ; **d)** M. W. Cronyn and E. Zavarin, J. Org. Chem., 19, 139 (1954) ; **e)** P. L. Fuchs and P. R. Hamann, J. Org. Chem., 48, 914 (1983) ; **f)** K. C. Nicolaou, D. A. Claremon, D. P. Papahatjis and R. L. Magolda, J. Am. Chem. Soc., 103, 6969 (1981) ; **g)** P. Charbades, J. P. Decor and J. Varagnat, Tetrahedron, 33, 2799 (1977) ; **h)** P. S. Manchand, M. Rosenberger, G. Saucy, P. A. Wehrli, H. Wong, L. Chambers, M. P. Ferro and W. Jackson, Helv. Chim. Acta, 59, 387 (1976) ; **i)** B. M. Trost and R. W. Warner, J. Am. Chem. Soc., 104, 6112 (1982) ; **j)** C. Fehr, Helv. Chim. Acta, 66, 2519 (1983) ; **k)** C. Mercier, Thèse de Docteur-Ingénieur, Paris VI, 1984 ; **12. a)** D. E. O'Connor and W. I. Lyness, J. Am. Chem. Soc., 86, 3840 (1964) ; **b)** I. Sataty and C. Y. Meyers, Tetrahedron Letters, 4161 (1974) ; **c)** J. Hine, S. Linden, A. Wang and V. Thiagarajan, J. Org. Chem., 45, 2821 (1980) ; **13.** C. Hervé du Penhoat and M. Julia, accepted at Tetrahedron ; **14.** B. Akermark, J. E. Nyström, T. Rein, J. E. Bäckvall, P. Helquist and R. Aslanian, Tetrahedron Letters, 25, 5719 (1984) ; **15. a)** See references 9f and 9i ; **b)** M. Mulhauser, Thèse de Docteur-Ingénieur, Paris VI, 1983 ; **c)** P. Chabardes, M. Julia and A. Menet, C. A. 80 : 26750 w - Ger. Off. 2, 319, 783 (CI.C07c) and C. A. 79 : 126671 u - Ger. Off. 2, 305, 215 (CI. C07c) ; **d)** S. Halazy and P. Magnus, Tetrahedron Letters, 25, 1421 (1984) ; **16.** J. J. Burger, T.B.R.A. Chen, E.R. de Waard and H. O. Huisman, Tetrahedron, 37, 417 (1981) ; **17.** L.E Overman, C.B. Petty, TakashiBan and G.T.Huang, J. Am. Chem. Soc., 105, 6335 (1983) ; **18. a)** R.V.C. Carr and L. A. Paquette, J. Am. Chem. Soc., 102, 853 (1980) ; **b)** O. de Lucchi and G. Modena, Tetrahedron Letters, 24, 1653 (1983) ; **c)** L. A. Paquette and W. A. Kinney, Tetrahedron Letters, 23, 131 and 5127 (1982) ; **d)** L. A. Paquette and G. D. Crouse, J. Org. Chem., 48, 141,(1983) ; **19.** G. Maccagnani, F. Montanari and F. Taddei, J. Chem. Soc., B, 453 (1968) ; **20. a)** K. N. Houk, J. Am. Chem. Soc., 95, 4092 (1973) ; **b)** J. Sauer and R. Sustmann, Angew. Chem. Internat. Edn., 19, 779 (1980) ; **21.** D. Babin, J.D. Fourneron and M. Julia, Bull. Soc. Chim. France, II, 588 (1980) ; **22.** S.C. Watson and J.F. Eastham, J. Organometallic Chem., 9, 165 (1967); **23.** R.B. Moffett in "Organic Syntheses" Vol. IV, John Wiley & Sons, New York, 1963, p. 238.