Tetrahedron Vol. 42, No. 17, pp. 4807 to 4816, 1986
Printed in Great Britain.

0040-4020/86 $3.00+.00

SYNTHESIS WITH SULFONES XLIV. STEREOSELECTIVE PREPARATION OF EE 1,3-DIENES BY ELIMINATION OF BENZENESULFINIC ACID FROM E HOMOALLYLIC SULFONES.

C. HERVE DU PENHOAT and M. JULIA *

Laboratoire de Chimie, Ecole Normale Supérieure, 24, rue Lhomond, 75231 PARIS CEDEX 05 - FRANCE.

(*Received in France* 25 *June* 1986)

ABSTRACT : *The preparation of pure E and Z homoallylic 1,1-disulfones followed by the stereoselective reduction of one sulfonyl moiety afforded pure E and Z homoallylic sulfones respectively. Basic elimination with tBuOK in THF gave the corresponding 1,3-dienes in good yield. This reaction, highly stereoselective in the case of E homoallylic sulfones, has been used in the synthesis of (8E,10E) 8,10-dodecadienol, 10 and (9E)9,11-dodecadienol, 15, insect pheromone components.*

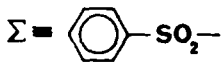
In the past few years much work has been devoted to the stereoselective preparation of 1,3-dienes (1a) often motivated by insect pheromone synthesis (1b,c).

We recently obtained 1,3-dienes by stereoselective reduction of the sulfonyl moiety of 2-phenylsulfonyl 1,3-dienes (2) which were prepared from readily available E allylic sulfones (3). An alternate approach to 1,3-dienes would be the basic elimination of benzenesulfinic acid from homoallylic sulfones.

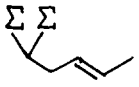
It is known that for saturated sulfones this reaction requires severe conditions and is not stereoselective (4). However, in the case of polyenic (5a-h) and homopropargylic (5i) substrates, elimination has been achieved under relatively mild conditions, aliphatic sulfones leading to E olefins. The object of the present work was to investigate the elimination reaction of simple homoallylic sulfones.

In order to study the scope and the stereochemistry of this reaction we required both pure E and Z homoallylic sulfones. Homoallylic 1,1-disulfones were suitable precursors as it has been shown that unsaturated 1,1-disulfones, easily purified by recrystallization, undergo stereoselective reduction of one sulfonyl moiety (3). Thus, bisbenzenesulfonylmethane 1 was treated with sodium hydride in DMF followed by technical crotylbromide to yield 85% of 2 as well as 12% of unchanged 1. The crude product contained the same 75/25 mixture of E and Z isomers as the starting halide as evidenced by ^{1}H NMR at 250MHz. Successive recrystallizations (7-8) afforded in 33% yield a compound 2E of stereochemical purity above 99%. Reductive cleavage of this material yielded monosulfone 4E containing less than 1% of the Z isomer, as shown by HPLC.

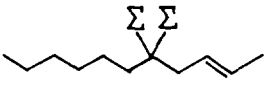
Alkylation of 2E with hexyliodide followed by recrystallization of the crude product led to 55% of 3E as well as 6% of unchanged 2E, Table 1 entry 1. Here again the stereoisomers could be distinguished by ^{1}H NMR and 3E was at least 98%E. Reduction of the 1,1-disulfone with aluminium amalgam (3) afforded 88% of 5E.



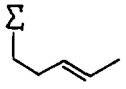
1



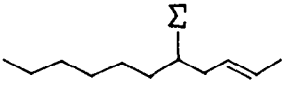
2 E



3 E

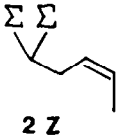


4 E

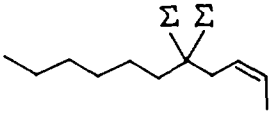


5 E

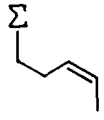
6 E E



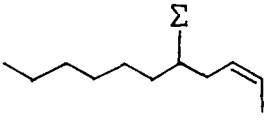
2 Z



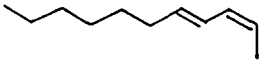
3 Z



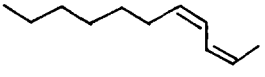
4 Z



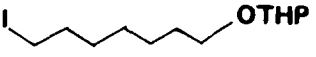
5 Z



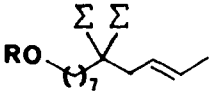
6 Z E



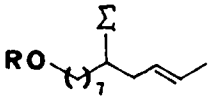
6 Z Z



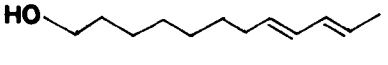
7



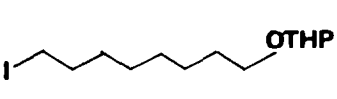
8



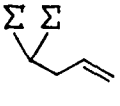
9



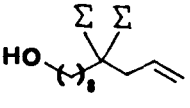
10



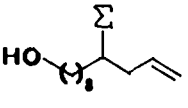
11



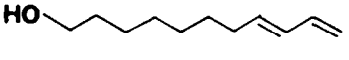
12



13

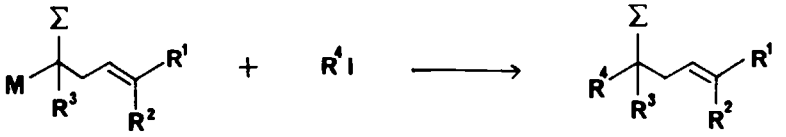


14



15

TABLE 1 : ALKYLATION OF METALATED HOMOALLYLIC 1,1-DISULFONES AND SULFONES WITH ALKYLIODIDES



Entry	Starting Disulfone or Sulfone [a] Compound mmol(g)	R^1	R^2	R^3	Iodide R^4 mmol(g)	Conditions Base(equiv.);Solvent(ml) 0°C ; Time	Alkylated Disulfones or Sulfone [a] Compound (Yield %)	m.p.°C (ethanol)	Elemental Analysis [b]	Other Products (%)
1	2E 10(3.50)	Me	H	Σ	n-Hex 14 (3.00)	NaH(1.05); DMF(30°); 80°; 2h	3E (55)	94	$C_{23}H_{30}O_4S_2$	2E (6)
2	2Z 2(0.700)	H	Me	Σ	n-Hex 2.4 (0.509)	NaH(1.2); DMF(10); 80°; 5h	3Z (82)	68-70	$C_{23}H_{30}O_4S_2$	2Z (13)
3	4Z 0.88(0.184)	H	Me	H	n-Hex 1.06(0.225)	n-BuLi(1.05); THF(4.5); -10°, 1h ; +10°, 2h	--			4Z, X [c] (53)
4	2E 20(7.00)	Me	H	Σ	$-(CH_2)_7OTHP$ 20(6.52)	NaH(1.05); DMF(100); 80°; 5h	8E, R=H (46)		$C_{24}H_{32}O_5S_2$	2E (29)
5	12 13(4.37)	H	H	Σ	$-(CH_2)_8OTHP$ 15(5.1)	NaH(1.05); DMF(100); 80° ; 15h	13E (33)		$C_{24}H_{32}O_5S_2$	12E (23)
6	4E 3(0.63)	Me	H	H	$-(CH_2)_7OTHP$ 3.1 (1.0)	n-BuLi(1.05); THF(15); -30°; 15h	9E, R=THP (97)			

[a] Unique double-bond configuration according to ^1H NMR at 250MHz [b] see Table 6 [c] ~76mg of unidentified sulfones.

It should be noted that in the case of homoallylic sulfone, 9E, a 70% yield was obtained by first reducing 2E to 4E followed by metallation with n-BuLi in THF and alkylation with the alkyliodide instead of 48% by the other route (entries 4 and 6, Table 1, 1 and 5, Table 2).

The homoallylic sulfone 5Z was prepared in a similar way from Z-crotyl bromide (obtained from commercially available 2-butyn 1-ol according to literature procedures (6)). Condensation of the halide with bisbenzenesulfonylmethylsodium afforded 73% of 2Z (98% pure) according to ^{1}H NMR. The 1,1-disulfone was alkylated with hexyliodide to give 82% of 3Z, Table 1, entry 2, which was reduced with Al-Hg to give 91% of 5Z. Following the alternate route, reduction of 2Z gave the monosulfone 4Z but attempted alkylation of 4Z under conditions used for 4E did not lead to 5Z, Table 1, entry 3. Instead 53% of 4Z was recovered as well as unidentified sulfones. Z homoallylic sulfones have been prepared previously by addition of a vinyl cuprate to benzenesulfonylethylenes (7).

Elimination of benzenesulfinic acid from 5E was achieved by stirring for an hour at room temperature with 2 equivalents of t-BuOK in THF (5ij,20). 2,4-Undecadiene was formed in 65% yield and only the EE isomer could be detected by ^{1}H NMR in comparison with spectra of all 4 isomers (8). Capillary GLC-mass analysis indicated the presence of 2 minor isomers, 2.5% and 1.6% respectively.

When treated as above 5Z was recovered unchanged, Table 3, entry 2. However, at reflux temperature elimination proceeded smoothly to yield 74% of 2,4-undecadienes 6. This time the isomeric ratio was 84/11/5 2Z,4E/2Z,4Z/2E,4E according to GLC-mass analysis and ^{1}H NMR at 250MHz confirmed a 85/10/5 mixture of ZE,ZZ and EE isomers. Shortening the reaction time gave similar results indicating that isomerization of 6 (9) was negligible under these conditions.

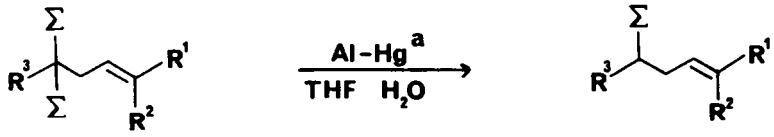
In light of a recent review of E2 reactions (9a) the stereoselectivity observed in the case of sulfone 5E is quite remarkable. Indeed, homoallylic substrates bearing common leaving groups (Cl,Br,OTs) undergo elimination with low stereoselectivity (65-85% of the E isomer) under fairly similar conditions (t-BuOH-t-BuOK). Chabardès (5b) evoked E2 syn elimination on heterogeneous base (i-PrOK in toluene) to explain the excellent stereoselectivity observed with a homoallylic sulfone precursor of vitamin A. However, from recent reports in the literature (5c) as well as results obtained in this laboratory (5f,g) it is clear that homogeneous conditions also give stereoselective elimination.

In the case of the Z homoallylic sulfone 5Z elimination is less stereoselective (85%) but isomerization of the existing double bond is just barely significant, ~4%.

Randomization of this double bond would only be expected in the case of a very sluggish elimination reaction as recent studies have shown that allylic potassium compounds in THF lose their stereochemistry slowly on the NMR time scale (10). The explanation for the highly stereoselective elimination of E homoallylic sulfones will require furthur studies. A "bad" leaving group such as benzenesulfinate ion would lead to a late E_2 transition state in the variable transition state theory of J.F. Bunnett (9b) so that the eclipsing effects in the cis olefin would be much more strongly felt than in the early transition states corresponding to the "better" leaving groups.

As it appeared that elimination of sulfinic acid from E homoallylic sulfones was a convenient approach to EE conjugated dienes we undertook the preparation of two insect pheromone components.

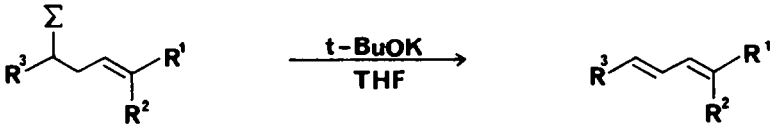
TABLE 2 : REDUCTION OF A PHENYLSULFONYL GROUP OF HOMOALLYLIC 1,1-DISULFONES



Entry	1,1-Disulfone [b] Compound mmol(g)	R^1	R^2	R^3	Homoallylic Sulfone Compound [b] (yield)	Elemental Analysis [c]
1	2E 10(3.50)	Me	H	H	4E [d] (95)	$C_{11}H_{14}O_2S$
2	2Z 2(0.70)	H	Me	H	4Z (96)	$C_{11}H_{14}O_2S$
3	3E 10(4.34)	Me	H	n-Hex	5E (88)	$C_{17}H_{26}O_2S$
4	3Z 1.5(0.651)	H	Me	n-Hex	5Z (91)	$C_{17}H_{26}O_2S$
5	8E 42.3(4.64)	H	Me	$(CH_2)_7OH$	9E, R=H (72)	$C_{18}H_{28}O_3S$
6	13E 3.88(1.80)	H	H	$(CH_2)_8OH$	14E (89)	$C_{18}H_{28}O_3S$

[a] 19ml of THF, 1ml of H_2O and 400mg(~15equiv.) of Al-Hg(per mmol of substrate). [b] Unique double-bond configuration according to ^1H NMR at 250MHz (> 98%). [c] See Table 6 . [d] 99/1 by HPLC (eluent : 2,2,4-trimethylpentane/ethylacetate : 90/10 : λ=265nm ; 2 Du Pont Zorbax Sil. (4.6mmx25cm) columns in series).

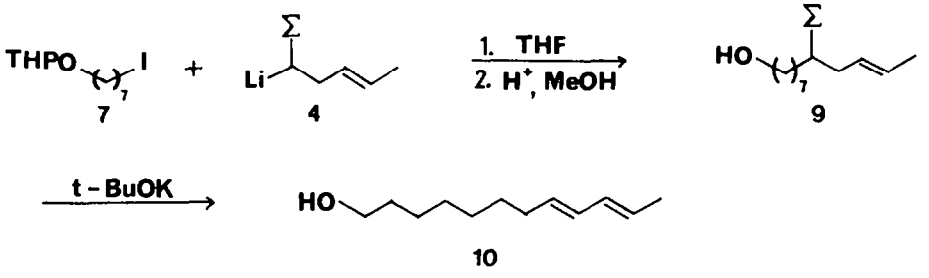
TABLE 3 : 1,2-ELIMINATION OF BENZENESULFINIC ACID FROM HOMOALLYLIC SULFONES



Entry	Sulfone Compound mmol(g)	R^1	R^2	R^3	Conditions °C	Time h	Diene Compound (% yield)	Isomer Ratio % [a]		
1	5E	Me	H	n-Hex	20	1	6 (65)	96(EE)	2.5	1.6
2	5Z	H	Me	n-Hex	65	1	6 (74)	84(ZE)	11(ZZ)	5(EE)
3	9	Me	H	$(CH_2)_7OH$	20	1	10 [b] (35)			
4	"	"	"	"	"	3	10 [c] (32)			
5	"	"	"	"	60	1	10 (74)	97.6(EE) [d]	2.4(EZ) [d]	
6	14	H	H	$(CH_2)_8OH$	20	1.7	15 (85)	95(E) [e]		

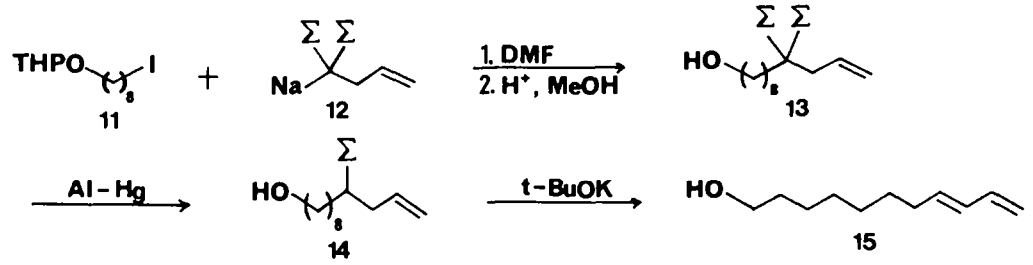
[a] Capillary GLC and ^1H NMR at 250MHz see experimental section. [b] Also 46% of unchanged 9. [c] Also 32% of unchanged 9. [d] Capillary-GLC in comparison with samples of E8,E10 10 and E8,Z10 10 (12). [e] Capillary-GLC in comparison with a sample of 9E11 15 (12).

Thus 1,7-heptanediol was converted into 1-iodo 7-(tetrahydro-2H-pyranyl-2-oxy)heptane 7 by a known method (11). Condensation with the lithio derivative of 4E followed by deprotection of the alcohol yielded 97% of sulfone 9 R=H, 98%E by ^{1}H NMR at 250MHz. Elimination under the usual conditions with t-BuOK in THF was slow at room temperature, Table 3, entries 4-5, but proceeded smoothly at 60° to give 74% of 8,10-dodecadiene-1-ol, 10, pheromone component of *Laspeyresia pomonella L.*, the codling moth. The major component was shown to be E8, E10 10 by ^{1}H NMR. Capillary-GLC indicated that the producted contained 97.6% of E8, E10 10 and 2.4% of E8-Z10 10.



In a similar way, 1,8-octanediol was converted into 1-iodo 8-(tetrahydro- 2H-pyranyl-2-oxy) octane 11 (11). Condensation with the sodio derivative of 1,1-disulfone 12 yielded 33% of 13 as well as 23% of unchanged 12 after removal of the ether group. Reduction of 13 led to 89% of monosulfone 14 which was transformed into 9,11-dodecadiene 1-ol, 15, in 85% yield with t-BuOK. Only the E isomer was observed by ^{1}H NMR at 250MHz.

Most of the early syntheses of 10 and 15 have been reviewed by Rossi (13). Recent techniques with better than 95% stereoselectivity are given in ref. 14. The overall yields, (30-70%), the complexity of starting materials, and the simplicity of experimental procedures vary greatly. Elimination of sulfinic acid from E homoallylic sulfones should complement these approaches to EE conjugated dienes.



EXPERIMENTAL

Elemental analyses ($C_nH_nS_n$ signifies 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 a 50/45/5 eluent of cyclohexane, dichloromethane and ethylacetate. A pentane/ether gradient was used for vacuum chromatography (15)(Merck 60H silica gel) Capillary VPC were performed on the following columns : CPSIL 5 (0.1*m* ; 50m x 0.25mm) for 6, and CPWAX 57 (0.2μ ; 25m) for 10 and 15 (12).

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

All solvents were distilled over appropriate reagents : benzophenone- sodium (THF, ether), P_2O_5(pentane, cyclohexane,DMF), calcium hydride (CH_2Cl_2, $CHCl_3$). t-BuOK was prepared from potassium and freshly-distilled t-butanol (16) and used without subliming. n-Butyllithium was titrated prior to use with a 1N solution of benzylic alcohol in toluene using 2,2'-biquinoline (17) as the indicator. All reactions were run under a positive pressure of dry nitrogen.

Spectral data are collected in Table 4 for sulfones and in Table 5 for all other compounds.

1,1'- 3-Pentenylidenebis(sulfonyl) bisbenzene 2E
(1,1-Bisbenzenesulfonyl-3E-pentene

An 80/20 E/Z mixture of compounds 2 was prepared by metallation of bisbenzenesulfonylmethane (18,3)(NaH/DMF) followed by alkylation with crotylbromide (Fluka-a 64/16/20 mixture of E 1-bromo-2-butene, Z 1-bromo-2-butene and 3-bromo- 1-butene)(85%). Several recrystallizations from ethanol afforded pure 2E (m.p. 86°C) as evidenced by ^{1}H NMR at 250MHz (33% from 1).

1,1'- 3-Pentenylidenebis(sulfonyl) bisbenzene 2Z
(1,1-Bisbenzenesulfonyl-3Z-pentene

A solution of 2.847g (40.7mmol) of 2-butyne-1-ol (Aldrich) in 20ml of ethanol was refluxed with 30g of Zn-$CuSO_4$ for 15h according to a known procedure (6a,b). After filtering over Celite and drying, distillation yielded 1.4g (50%) of pure Z crotylalcohol (b.p. 122-23°C) as evidenced by VPC (OV 101, 2.5mx3mm). A stirred solution of 1.025g(14.6mmol) of Z crotylalcohol in 30ml of ether was treated with 0.54ml(0.38 equiv.) of PBr_3 at 0°C (6d). The temperature was allowed to rise to 13°C and stirring maintained for a total of 1.5h. The reaction mixture was poured over a mixture of ice and water and the aqueous layer extracted with ether. The combined organic layers were washed with a 10% aqueous solution of sodium carbonate followed by water. After drying most of the ether was removed by distillation over a glass-bead column (30cmx2cm). ^{1}H NMR analysis of a small portion of the residue in the presence of toluene as an internal standard indicated a 78% yield of Z-crotylbromide. This residue was then treated with a solution of 11 mmol of bisbenzenesulfonylmethylsodium in 30ml of DMF as described below in the typical procedure for alkylating 1,1-disulfones. Workup and recrystallization from ethanol afforded 2.81g (73%) of 2Z, m.p. 98-100°C.

Typical Procedure for Alkylation of 1,1-Disulfones Table 1

1,1' 2-Butenylheptylidenebis(sulfonyl) bisbenzene 3E (5,5-bisbenzenesulfonyl-2E-undecene)

A solution of 3.50g(10mmol) of 1,1-disulfone 2E in 10ml of DMF was added dropwise to a stirred suspension of 1.05 equiv. of sodium hydride (460mg of 55% NaH gel rinced twice with pentane) in 10ml of DMF. The mixture was heated at 50°C for 15 minutes, cooled to room temperature and a solution of 3.00g(14mmol) of hexyliodide in 10ml of DMF was added dropwise. The reaction mixture was stirred at 80°C for 2h and monitored by TLC. The mixture was cooled and hydrolyzed with a saturated aqueous solution of ammonium chloride. The resulting mixture was extracted 5 times with dichloromethane and the combined organic layers were washed once with an aqueous saturated solution of sodium thiosulfate followed by 4 times with water. After drying and filtering the solvents were evaporated and the residue purified by vacuum chromatography. Recrystallization from ethanol of the major product yielded 2.39g (55%) of 3E. 210mg of 2E were recovered in another fraction (smaller R_f). Other alkylations were carried out in a similar way, using the parameters mentioned in Table 1.

In the case of compounds 8, 9 and 13 the tetrahyro-2H-pyran-2-yloxy protecting group was removed prior to purification by stirring with methanol (20ml/mmol of 1,1-disulfone) and 5 drops of concentrated HCl(10N) for 3h at room temperature.

Typical Procedure for Reductive Cleavage of One Phenylsulfonyl Group of Homoallylic-1,1-Disulfones Table 2

(2-Butenyl)heptylsulfonyl benzene 5E
(5-Benzenesulfonyl-2E-undecene)

2.70g(0.1mol) of aluminum amalgam was prepared according to a literature procedure (19,3) by plunging strips of aluminum foil (10cmx1cm) into an aqueous 2% solution of mercuric chloride for 30 seconds followed by rincing first in ethanol and then in ether. These strips were rapidly cut into squares and dropped into a stirred solution of 4.34g(10mmol) of 3E in 190ml of THF and 10ml of water. After 3h, another 1.5g of reducing agent were added and stirring was maintained for 2h. The suspension was filtered over Celite and the solvent evaporated at reduced pressure. The residue was diluted with ether, washed with water, dried and filtered. Evaporation of the solvent and vacuum chromatography yielded 2.59g(88%) of 5E as an oil.

Typical Procedure for 1,2-Elimination of Benzenesulfinic Acid From Homoallylic Sulfones Table 3

(2E, 4E)-Undecadiene 6

0.560g(5equiv.) of potassium t-butoxide were added to a stirred solution of 0.294g (1mmol) of 5E in 10ml of THF (20,5i). After 1h, 5ml of water were added and the THF was evaporated. The residue was extracted with ether, washed with water dried and filtered. The solvent was distilled through a glass-bead column (30cmx2cm) and the residue purified by vacuum chromatography to yield 99mg (65%) of 6. The isomer ratio was determined by capillary-VPC-mass. Structural assigment was made by comparison of the ^{1}H NMR spectrum at 250MHz with those of all four isomers (8).

Typical Procedure for Alkylating Homoallylic Sulfones Table 1 (entries 3 and 6)

(1-Tetrahydropyranyloxy-8 benzenesulfonyl-10E-dodecene 9, R=THP

A stirred solution of 0.630g(3mmol) of sulfone 4E in 15ml of THF was cooled to -65°C and 2.3ml(1.05equiv.) of n-butyllithium (1.3N in hexane) were added dropwise (21). The

Table 4 : m/e and ^1H NMR spectra of sulfones and 1,1-disulfones.

Compound	IR	m/e	^1H NMR at 250MHz in $CDCl_3$ (δ=7.27ppm for residual $CHCl_3$)
2E	1325, 1305, 1150, 975	351, 209, 143, 141, 125	1.49(br d,3H,5), 2.83(m,2H), 4.44(t,1H,6), 5.24 to 5.45(m,2H,J_{AB}=15.5), 7.51 to 7.72(m,6H), 7.9 to 7.98(m,4H)
2Z		351, 209, 143, 141, 125	1.42(dd,3H,J_1=7,J_2=1.2), 2.87(br t,2H,J=6.2), 4.45(t,1H,6.4), 5.32 to 5.47(m,2H,J_{AB}=11), 7.53 to 7.62(m,4H), 7.65 to 7.75(m,2H), 7.92 to 8.01(m,4H)
3E	1315, 1155	435, 309, 293, 223, 167	0.83(t,3H,6.7), 1.11 to 1.29(m,6H), 1.51 to 1.7(m,5H containing a doublet at 1.66ppm, J=4.5), 2.04 to 2.16(m,2H), 2.95(m,2H), 5.49 to 5.70(m,2H,J_{AB}=15), 7.54 to 7.65(m,4H), 7.65 to 7.76(m,2H), 8 to 8.10(m,4H)
3Z		435, 293, 167, 143, 141, 125	0.83(t,3H,6.7), 1.14 to 1.31(m,6H), 1.45 to 1.69(m,5H containing a br doublet at 1.55ppm, J 4.8), 2.11 to 2.21(m,2H), 2.94(m,2H), J 4.8), 2.11 to 2.21(m,2H), 2.94(m,2H), 5.56 to 5.79(m,2H,J_{AB}=10.5), 7.54 to 7.66(m,4H), 7.66 to 7.78(m,2H), 8.04 to 8.14(m,4H)
4E	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)
4Z		211, 143, 125	1.44(br d,3H,7), 2.35(br q,2H,7.8), 3.04(m,2H), 5.13 to 5.27(m,1H), 5.35 to 5.51(m,1H,J_{AB}=11), 7.48 to 7.66(m,3H), 7.83 to 7.92(m,2H)
5E	1305, 1150, 970	295, 152, 143, 125	0.8(t,3H,6.7), 1.08 to 1.65(m,12H containing a br doublet at 1.56 ppm, J_1=6,J_2=1), 1.68 to 1.85(m,1H), 2.23(quintuplet,1H,7.5), 2.48(m,1H), 2.89(tt,1H,J_1=7.5,J_2=4.8), 5.28(m,1H,J_{AB}=15), 5.43(m,1H,J_{AB}=15), 7.47 to 7.69(m,3H), 7.83 to 7.92(m,2H)
5Z		295, 219, 209, 169, 161, 160, 152, 143, 125	0.79(t,3H,6.7), 1.1 to 1.63(m,12H containing a br doublet at 1.50ppm, J=7), 1.73 to 1.89(m,1H), 2.32(quintuplet, 1H,7.8), 2.50(m,1H), 2.93(tt, 1H,J_1=7.5,J_2=4.8), 5.23 to 5.37(m,1H,J_{AB}=11), 5.44 to 5.6(m,1H,J_{AB}=11), 7.52 to 7.7(m,3H), 7.86 to 7.94(m,2H)
8E	3400, 1310, 1150, 1070, 970	465, 414, 341, 323, 163	1.13 to 1.34(m,6H), 1.44 to 1.69(m 8H, containing a br doublet at 1.66 ppm, J=5), 2.05 to 2.15(m,2H), 2.94(br d,2H,5), 3.6(t,2H,6.5), 5.47 to 5.67(m,2H,J_{AB}=16), 7.53 to 7.64(m,4H), 7.64 to 7.74(m,2H), 8 to 8.07(m,4H)
9E, R=H	3400, 1300, 1150, 1090, 970	325, 307, 182, 164, 143, 135, 125	1.15 to 1.64(m,16H, containing a dd at 1.57ppm, J_1=6.2, J_2=1), 1.71 to 1.85(m,1H), 2.25(dt,1H,J_1=15, J_2=7.5), 2.48(m,1H), 2.9(tt,1H,J_1=7.5, J_2=5), 3.60(t,2H,6.6), 5.22 to 5.36(m,1H,J_{AB}=15), 5.44(br dq,1H,J_1=15, J_2=6.2), 7.53 to 7.7(m,3H), 7.85 to 7.93(m,2H)
9E, R=THP			1.10 to 2.73(m,23H), 2.87 to 3.23(m,1H), 3.23 to 4.13(m,4H), 4.62(br s,1H), 5.13 to 5.73(m,2H), 7.5 to 8.07(m,5H)
12			2.89(m,2H), 4.49(t,1H,J=6), 4.95 to 5.06(m,2H), 5.79(ddt,1H,J_1=17, J_2=10.2, J_3=6.7), 7.51 to 7.62(m,4H), 7.62 to 7.73(m,2H), 7.92 to 8(m,4H)
13	3400, 1315, 1150, 1070	323, 209, 181, 163, 143, 141, 125	1.10 to 1.33(m,9H), 1.42 to 1.7(m,6H), 2.07 to 2.17(m,2H), 3.0(br d,2H, 6.5), 3.59(t,2H,6.6), 5.16 to 5.28(m,2H), 6.01(ddt,1H,J_1=17, J_2=11, J_3=6.5), 7.54 to 7.65(m,4H), 7.65 to 7.76(m,2H), 8.02 to 8.1(m,4H)
14	3400, 1300, 1145,1085	325, 307, 183, 143, 125	1.10 to 1.61(m,14H), 1.69 to 1.85(m,1H), 2.28(br quintuplet,1H,7.5), 2.47 to 2.59(m,1H), 2.93(tt,1H, J_1=7.5, J_2=5), 3.57(t,2H,6.5), 4.99 (m,1H), 5.04(t,1H,1), 5.61 to 5.78(m,1H), 7.5 to 7.69(m,3H), 7.83 to 7.90(m,2H)

TABLE 5 : m/e and ^1H NMR of conjugated alkadienes and ω-functionalized compounds

Compound	m/e	^1H NMR at 250MHz in $CDCl_3$ (δ=7.27ppm for residual $CHCl_3$)
6EE	153(3), 152(25), 123(1), 110(3), 109(3), 96(3), 95(10), 94(1), 93(2), 91(3), 83(1), 82(14), 81(72), 80(6), 79(31), 78(2), 77(11), 69(8), 68(100)	0.86(t,3H,7), 1.14 to 1.41(m,8H), 1.71(d,3H,6.5), 2.02(q,2H,7), 5.5 to 5.64(m,2H), 5.94 to 6.08(m,2H)
6 ZE (84) + 6 ZZ (13)	153(2), 152(15), 123(1), 110(2), 109(2), 96(2), 95(7), 93(1), 91(3), 83(1), 82(11), 81(54), 80(6), 79(37), 78(3), 77(15), 69(8), 68(100) 153(2), 152(17), 123(1), 110(3), 109(3), 96(3), 95(9), 91(3), 82(13), 81(47), 80(5), 79(33), 78(2), 77(13), 69(8), 68(100)	0.87(t,3H,7), 1.17 to 1.47(m,8H), 1.74(dd,3H,J_1=7, J_2=1.5), 2.03 to 2.22(m,2H containing a quartet at 2.03, J=7), 5.39(dq,~0.85H, J_1=11, J_2=7), 5.48 to 5.61(m,0.3H), 5.69(dt,~0.85H, J_1=11, J_2=7), 6(br tm, 0.90H, J_1=11, J_2=1.5), 6.35(m,~1.15H containing a br ddm, J_1=15, J_2=11, J_3=1.2)
7		1.12 to 2.03(m,16H), 3.15(t,2H,6.6), 3.27 to 4.0(m,4H), 4.55(m,1H)
10	225(2), 224(8), 164(3), 136(3), 135(12), 122(4), 121(15), 109(3), 108(8), 107(12), 97(3), 96(20), 95(17), 94(26), 93(27), 82(35), 81(100)	1.17 to 1.44(m,8H), 1.44 to 1.78(m,6H containing a doublet at 1.68ppm, J=6.5), 2.0(q,2H,6.7), 3.6(t,2H,6.5), 5.47 to 5.66(m,2H), 5.91 to 6.08(m,2H)
11		1.21 to 2.24(m,18H), 3.2(t,2H,6.8), 3.33 to 4.07(m,4H), 4.62(m,1H)
15		1.16 to 1.57(m,10H), 1.75(br s,1H), 2.02(q,2H,7), 3.59(t,2H),6.6), 4.92(br dd,1H, J_1=10.2, J_2=1.8), 5.05(br dd,1H, J_1=17, J_2=1.8), 5.68(dt,1H, J_1=15, J_2=7), 6.02(br dd,1H, J_1=15, J_2=10.2), 6.29(dt,1H, J_1=17, J_2=10.2)

Table 6 : Elemental Analysis.

Compound	Molecular Formulae	Calculated % C	H	S	Observed % C	H	S
2E	$C_{17}H_{18}O_4S_2$	58.29	5.14	18.29	58.43	5.15	18.00
2Z	$C_{17}H_{18}O_4S_2$	58.29	5.14	18.29	58.23	5.07	18.17
3E	$C_{23}H_{30}O_4S_2$	63.59	6.91	14.75	63.43	6.73	14.86
3Z	$C_{23}H_{30}O_4S_2$	63.59	6.91	14.75	63.37	7.04	14.50
4E	$C_{23}H_{30}O_4S_2$	62.86	6.67	15.24	62.68	6.82	15.12
4Z	$C_{11}H_{14}O_2S$	62.86	6.67	15.24	62.72	6.79	15.16
5E	$C_{17}H_{26}O_2S$	69.39	8.84	10.88	69.37	8.95	10.65
5Z	$C_{17}H_{26}O_2S$	69.39	8.84	10.88	69.44	8.84	10.68
8	$C_{24}H_{32}O_5S$	62.07	6.90	13.79	61.88	7.17	13.74
9	$C_{24}H_{32}O_5S$	66.66	8.64	9.88	66.54	8.77	9.88
12	$C_{18}H_{28}O_3S_2$	57.14	4.76	19.05	57.32	4.85	18.97
13	$C_{16}H_{16}O_4S_2$	62.07	6.90	13.79	62.01	7.04	13.88
14	$C_{24}H_{32}O_5S_2$	66.66	8.64	9.88	66.59	8.70	9.69
	$C_{18}H_{28}O_3S$						

temperature was allowed to rise to 20°C for 0.5h and then brought down to -30°C. 1g(3.1mmol) of 7- (tetrahydro-2H-pyran-2-yl)oxy 1- iodoheptane 7 were added dropwise and the stirred solution was maintained at -30°C for 15h. The reaction mixture was hydrolyzed with a saturated aqueous solution of ammonium chloride and the solvent evaporated at reduced pressure. Dilution with ether, the usual workup and flash chromatography (22) yielded 1.187g(97%) of 9, R=THP.

1,1'- 3-Butenylidene bis(sulfonyl) bisbenzene 12
(1,1-Bisbenzenesulfonyl-3-butene)

8.88g(30mmol) of bisbenzenesulfonylmethane 1, 1.35g(1.05equiv.) of NaH gel(55%), 3ml(34mmol) of allylbromide and 100ml of DMF were treated as described in the typical procedure (3h,70°C). Recrystallization from ethanol yielded 7.26g(72%) of 12, m.p. 116-18°C, $C_{16}H_{16}O_4S_2$.

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. a) H.V. Brachel and U. Bahr in "Houben-Weyl, Methoden der Organischen Chemie". Bd. V/1c, Georg-Thieme-Verlag, Stuttgart, P.1, 1970. b) C.A. Henrick, Tetrahedron, 33, 1845 (1977). c) K. Mori in "The Total Synthesis of Natural Products", edited by J. ApSimon, Wiley, Interscience, 4, P.1. (1981)
2. a) T. Cuvigny, C. Hervé du Penhoat and M. Julia, Tetrahedron Letters, 24, 4315 (1983). b) T. Cuvigny, J.L. Fabre and C. Hervé du Penhoat, M. Julia, Tetrahedron Letters, 24, 4319 (1983).
3. T. Cuvigny, C. Hervé du Penhoat and M. Julia, Bull. Soc. Chim. Fr., II-43 (1982).
4. a) T.J. Wallace and J.E. Hofmann, J. Amer. Chem. Soc., 85, 2739 (1963). b) R.A. Bartsch and J.F. Bunnett, J. Amer. Chem. Soc., 91, 1376 and 1382 (1969). c) A.K. Colter and R.E. Miller, J. Org. Chem., 36, 1898 (1971).
5. a) 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). b) P. Chabardès, J.P. Décor and J. Varagnat, Tetrahedron, 33, 2799 (1977). c) K.C. Nicolaou, D.A. Claremon, D.P. Papahatjis and R.L. Magolda, J. Amer. Chem. Soc., 103, 6969 (1981). d) B.M. Trost and R.W. Warner, J. Amer. Chem. Soc., 104, 6112 (1982). e) C. Fehr, Helv. Chim. Acta, 66, 2519 (1983). f) C. Mercier, Thesis, Paris 1984. g) J.P. Duchesne, Thesis 1986, Paris in print. h) Société Des Usines Chimiques Rhône Poulenc, French Patent, May 19, 1971 (2.138.212). i) P.L. Fuchs and P.R. Hamann, J. Org. Chem., 48, 914 (1983). j) Similar results were obtained in this laboratory by A. Callipolitis.
6. a) R.M. Magid, O.S. Fruchey, W.L. Johnson and T.G. Allen, J. Org. Chem, 44, 359 (1979). b) R.G. Bergman, J. Amer. Chem. Soc., 91, 7405 (1969). c) For reduction with $H_2/Pd(BaSO_4)$ see W.E. Gore, G.T. Pearce and R.M. Silverstein, J. Org. Chem., 40, 1705 (1975) and L.F. Hatch and S.S. Nesbitt, J. Amer. Chem. Soc., 72, 727 (1950). d) R.V.M. Campbell, L. Crombie, D.A.R. Findley, R.W. King, G. Pattenden and D.A. Whiting, JCS Perkin I, 897 (1975).
7. a) A. Alexakis, G. Cahiez and J.F. Normant, J. Organometallic Chem., 177, 293 (1979). b) G. de Chirico, V. Fiandanese, G. Marchese, F. Naso and O. Sciacovelli, J. Chem. Soc., Chem. Comm., 523 (1981).
8. H.P. Dang and G. Linstrumelle, Tetrahedron Letters, 19, 191 (1978).
9. a) R.A. Bartsch and J. Zavada, Chem. Rev., 80, 453 (1980). b) J.F. Bunnett, Survey Prog. Chem., 5, 53 (1969).
10. D.H. O'Brien, C.R. Russell and A.J. Hart, Tetrahedron Letters, 37 (1976) and references therein.
11. a) W.R. Coleman and W.G. Bywater, J. Amer. Chem. Soc., 66, 1821 (1944). b) K.N. Campbell and A.H. Sommers in "Organic Synthesis", vol. III, p. 446 ; John Wiley and Sons, Inc., New York, 1955. c) J.C. Lapierre Armande and U.K. Pandit, Rec. Trav. Chim., Pays-Bas, 99, 87 (1980).
12. The authors like to thank C. Descoins of the Institut National de la Recherche Agronomique for GPC analysis of 10.
13. R. Rossi, A. Carpita and M. Grazia Quirici, Tetrahedron, 37, 2617 (1981).
14. a) G.R. Knox and I.G. Thom, J.C.S. Chem. Comm., 373 (1981). b) D. Jieh Shyh Tsai and D.S. Matteson, Tetrahedron Letters, 22, 2751 (1981). c) J.H. Babler and R.A. Haack, J. Org. Chem., 47, 4801 (1982). d) S. Ranganathan, Raaj Kumar and V. Maniktala, Synthetic Communications, 921 (1982). e) R. Bloch and J. Abecassis, Tetrahedron Letters, 24, 1250 (1983). f) E. Block and M. Aslam, J. Amer. Chem. Soc., 105, 6164 (1983). g) T. Hayashi, M. Yanagida, Y. Matsuda and T. Oishi, Tetrahedron Letters, 24, 2665 (1983). h) S. Yamada, H. Ohsawa, T. Suzuki and H. Takayama, Chemistry Letters, 1003 (1983). i) C-N. Hsiao and H. Shechter, Tetrahedron Letters, 25, 1219 (1984).
15. D. Babin, J.D. Fourneron and M. Julia, Bull. Soc. Chim. Fr., 1980, II-588.
16. A.J. Speziale, K.W. Ratts and D.E. Bissing in "Organic Synthesis", vol. V, John Wiley and Sons, New York, 361.
17. S.C. Watson and J.F. Eastham, J. Organometallic Chem., 9, 165 (1967).
18. M.W. Cronyn and E. Zavarin, J. Org. Chem., 19, 139 (1954).
19. E.J. Corey and M. Chaykovsky, J. Amer. Chem. Soc., 87, 1345 (1965).
20. M. Julia and D. Arnould, Bull. Soc. Chim. Fr., 746 (1973).
21. M. Julia and D. Uguen, Bull. Soc. Chim. Fr., 513 (1976).
22. W.C. Still, M. Kahn and A. Mitra, J. Org. Chem., 43, 2923 (1978).