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SYNTHESES WITH SULFONES XLVII : STEREOSELECTIVE ACCESS TO 1,3- AND 1,4-DIENES THROUGH HYDROGENOLYSIS OF BENZENESULFONYLDIENES. APPLICATION TO PHEROMONE SYNTHESIS.

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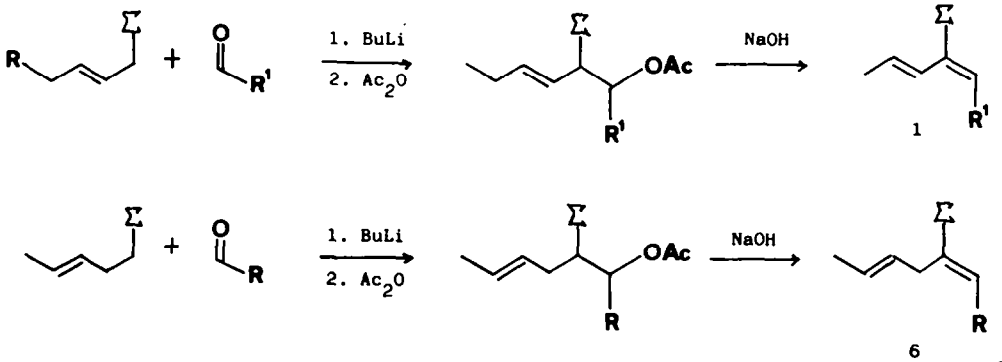
ABSTRACT : *The stereospecific reduction of EE 2-benzenesulfonyl-1,3-dienes to 2E 1,3-dienes with Grignard reagents under transition metal catalysis is described. Hydrogenolysis of the sulfonyl moiety of 2-benzenesulfonyl-1,4-dienes to 2E 1,4-dienes with sodium dithionite is reported. These techniques have been applied to the stereoselective synthesis of (7E, 9Z) dodecadienyl acetate 3d, (9Z, 11E) tetradecadienyl acetate 3e and (9Z, 12E) tetradecadienyl acetate, 6b.*

In the preceding papers [1] we reported the synthesis of EE 2-phenylsulfonyl-1,3- and 1,4-dienes from readily available E allylic [2] and homoallylic sulfones [3] respectively and aldehydes. These functionalized dienes, obtained with >95% stereoselectivity, are easily purified (>99.5% EE) by flash chromatography [4]. EE 1-Benzenesulfonyl-1,3-dienes were also prepared albeit in low yields by basic elimination of benzenesulfinic acid from allylic 1,1-disulfones [1]. In a preliminary note [5] we reported the stereospecific hydrogenolysis of the benzene sulfonyl group of 2-benzenesulfonyl-1,3-dienes with Grignard reagents under transition-metal catalysis leading to EZ 1,3-dienes. Full details of the stereospecific synthesis of 1,3- and 1,4- dienes from 1,3- and 1,4-dienes functionalized by the sulfonyl moiety are given here.



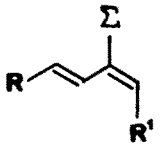
Several techniques have been recommended for the hydrogenolysis of vinylsulfones [6] to olefins. However only three reducing agents have been shown to be highly stereospecific : sodium dithionite [6a], Grignard reagents under transition-metal catalysis [6b] and aluminium amalgam [6cd]. The scope of the latter reaction, however, was shown [6c] to be limited.

Reduction of 2-benzenesulfonyl-1,3-dienes 1

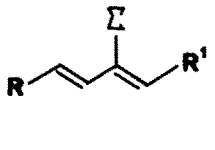
We first exposed dienesulfone 1a to aluminium amalgam [6c] and buffered sodium amalgam [6j] however the main product was the allylic sulfone 2a in 39% (also 55% of 1) and 100% yield respectively. We next tried sodium dithionite with phase transfer catalysis [6a]. In the case of vinylsulfones, the reaction has been shown to proceed by syn addition of the sulfoxylate ion followed by anti-elimination of sulfur dioxide and sulfinate ion from the intermediate sulfonylsul-

FORMULAE

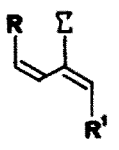
$\Sigma \equiv PhSO_2$



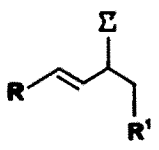
1 E E



1 E Z



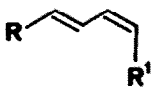
1 Z E



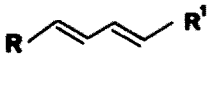
2

a R = R^1 = Et b R = Et, R^1 = n-Hex d R = $(CH_2)_6$ OTHP, R^1 = Et
e R = Et, R^1 = $(CH_2)_8$ OTHP

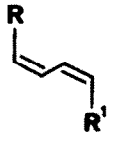
a R = R^1 = Et
b R = Et, R^1 = n-Hex
c R = Me, R^1 = n-Hex



3 E Z

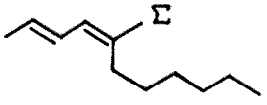


3 E E



3 Z Z

b R = Et, R^1 = n-Hex c R = Me, R^1 = n-Hex d R = $(CH_2)_6O\ R^2$, R = Et, e R^1 = Et, R^1 = $(CH_2)_8OR^2$
with R^2 = THP, H or Ac



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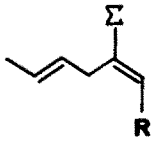

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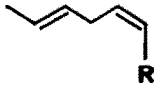

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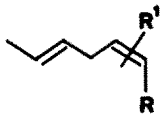

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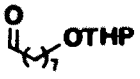
a R = n-Hex
b R = $(CH_2)_8$ OTHP

b R = $(CH_2)_8$ OR^2
with R^2 = THP, H or Ac

8



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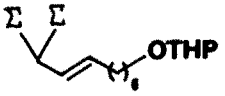

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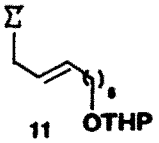

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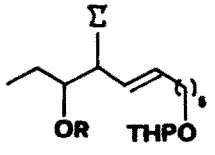
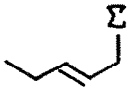


12

R = H or Ac



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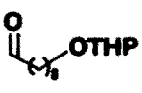

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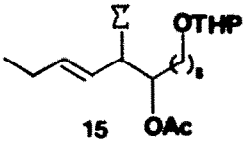

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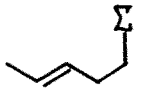

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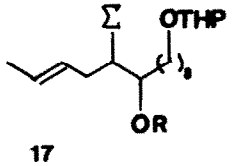
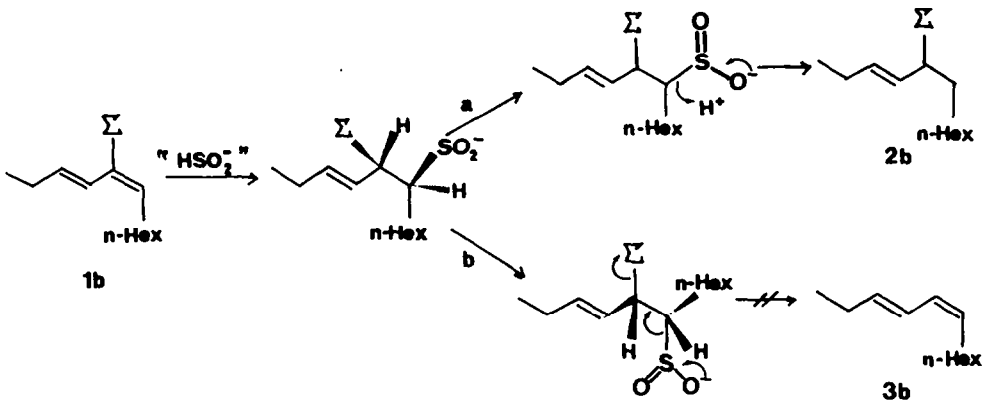


17

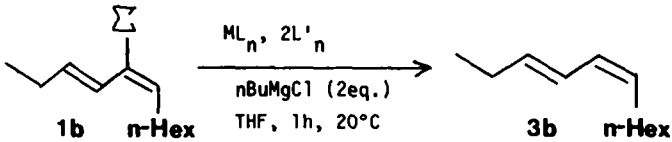
R = H or Ac

finate [6m]. Dienesulfone 1b disappeared rapidly while formation of the product, allylic sulfone 2b was slow (51%, 18h). Attempts to isolate the intermediate after methylation have so far failed [6f]. It thus appears that, in this case, protonation of the intermediate is more rapid than elimination.



We next turned to the recently reported stereospecific hydrogenolysis of vinylic sulfones with Grignard reagents in the presence of transition metals, which proved efficient for monoolefin synthesis [6b]. Reaction of 1b (>98.5% EE) with n-BuMgCl, 2% of $Pd(acac)_2$ and 4% of $n\text{-}Bu_3P$ led to dodecadiene 3b (40%) with however a notable (15%) loss of stereochemical purity as evidenced by ^1H NMR and capillary-glc. We checked that dienes 3b were not isomerized under those reaction conditions. However, isomerization did occur upon heating during evaporation of the solvents and therefore the catalyst must be carefully removed (see experimental) before isolation of the products.

Table 1 : Study of the stereospecificity of the reduction of [(1-butene-1-yl 1-octenyl)sulfonyl] benzene 1b with n-butylmagnesium chloride using various transition-metal catalysts.



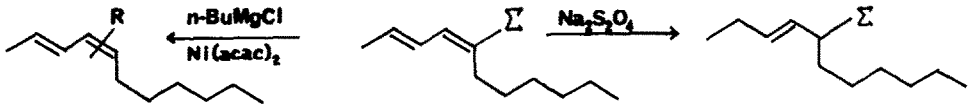
Entry	1 (a) Isomer Ratio			Reducing system		Yield	3 (b)(c)(d) Isomer Ratio			
				2 mol%	4 mol%					
	EE	EZ	ZE	MLn	2L'n	%	EZ	EE	ZZ	ZE
1	98.5	1	0.5	$Pd(acac)_2$	-	41	97	1		2
2	"	"	"	"	Dabco	39	97	1		2
3	"	"	"	"	nBu_3P	41	95	2		3
4	"	"	"	$(\eta^3\text{-}C_3H_5)_2Pd_2Cl_2$	PPh_3	35	93	3	1	4
5	"	"	"	$Ni(acac)_2$	-	51	96	4		
6	"	"	"	"	Dabco	46	97	3		
7	"			"	nBu_3P	45	97	3		
8	"	"	"	$NiCl_2(PPh_3)_2$	-	16 (e)	96	4		
9	3	96.5	0.5	$Ni(acac)_2$	-	23	10	90		
10	87	2	11	"	-	42	83	4	13	

a) %(EE+ZE) determined by hplc(±0.5%) and capillary-glc(±0.5%), %EZ determined by hplc (±0.5%) and capillary-glc (±0.5%), %ZE determined by ^1H NMR at 250MHz(±2%).
b) capillary-glc, internal standard, tridecane(glass column, Carbowax,90°C).
c) unidentified sulfones (m/z 472, M=1+3) also recovered. d) 0-3% of unidentified olefins also present. e) 51% of 1b was also recovered.

The reaction was carried out with various catalysts, Table 1. Palladium ones (entries 1-4) all gave acceptable (39-41%) yields of dodecadiene 3b EZ with high (93-97%) stereochemical purity. Several nickel catalysts were tried (entries 5-8) with slightly better yields (45-50%) and stereochemical purity (96-7%). The EZ-diene sulfone 1b (3% EE, 97% EZ) was hydrogenolysed to the EE diene 3b (10% EZ, 90% EE) in low (23%) yield. Similarly a mixture of EE and ZE dienesulfones 1b (77% EE, 5%EZ and 18%ZE) led to the corresponding EZ and ZZ diene 3b (75%EZ, 4%EE, 21%ZZ) in 40% yield thus indicating that this reduction is stereospecific.

Reduction of 1-benzenesulfonyl-1,3-diene 4

When 1-benzenesulfonyl-1E,3E-diene 4, prepared as previously described [1] was submitted to these conditions (2% $Ni(acac)_2$, 2eq.n-BuMgCl) about 15% of 3c(R=Me, R^1=n-Hex) containing 91% of the EZ isomer [7] were formed. Capillary-glc-mass analysis indicated that olefins with the molecular weight of cross-coupling products, M=3+C_4H_8, were also obtained in 10% yield. Under palladium catalysis, this reaction gave 26% of 3c (R=Me, R^1=n-Hex) but this time the major isomer, 67% was 3c EE. 8% of heavier olefins, M=3+C_4H_8, were also formed.



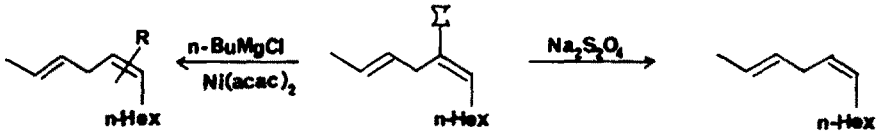
3c 4 2c

R = H 15%
R = n-Bu 10%

Here again reduction with $Na_2S_2O_4$ led to complete transformation of dienesulfone 4 but diene 3c (R=Me, R^1=n-Hex) could not be detected among the products. Allylic sulfone 2c (R=Me, R^1=n-Hex) formed in ~50% yield was identified by ^1H NMR of the crude product. As synthesis of 1,3-dienes 3 from dienesulfones 1 was more promising we did not pursue this approach.

Reduction of 2-benzenesulfonyl-1,4-diene 5

We next investigated the reduction of 2-benzenesulfonyl-1,4-dienes. Treatment of 5a (> 99% EE) with n-BuMgCl in the presence of 2% of $Ni(acac)_2$ led to 63% of a 81/19 mixture of 1,4-diene 6a and cross-coupling olefins 7a, (R^1=Bu). The stereochemical purity of 6a, determined by ^1H NMR, could only be evaluated as > 85% 7Z due to the signals of the other products. This time hydrogenolysis with sodium dithionite (2eq., 80°C, 3.25h) under phase transfer catalysis afforded 65% of 6a containing > 97% of EZ isomer. It should be noted that if the reaction was interrupted unchanged starting material and 1,4-diene 6 with abnormal stereoselectivity were recovered as if the intermediate had evolved in an unexpected way. However, the explanation for this phenomenum will require further studies.



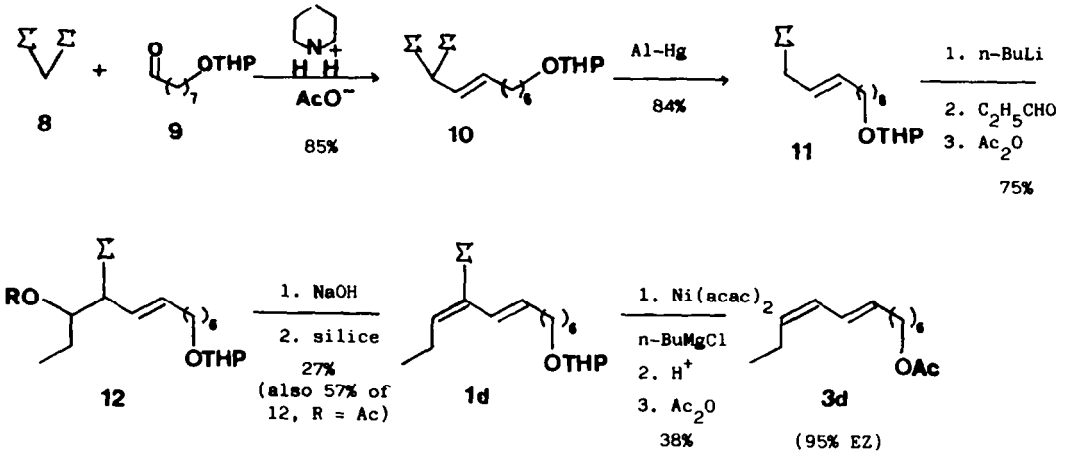
6a 51%
7a 12%

5a

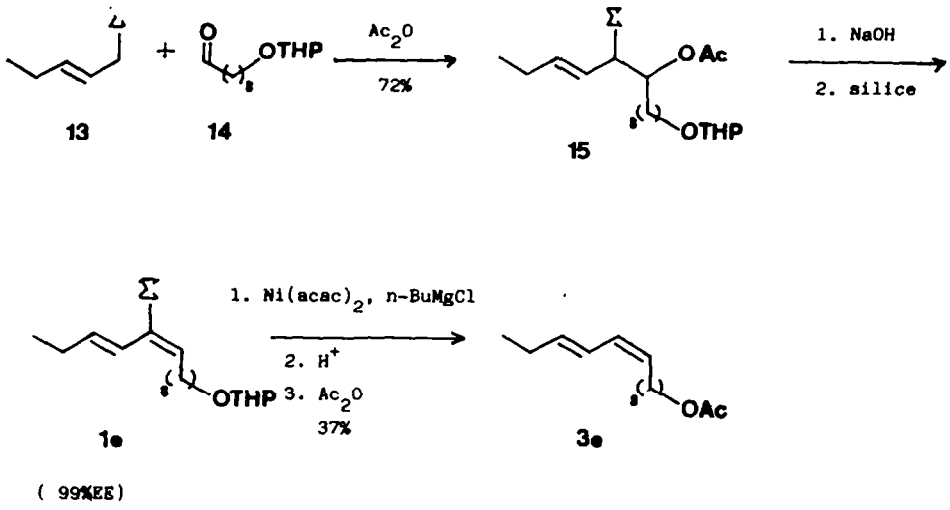
6a

Application to pheromone synthesis

As these new approaches to 1,3- and 1,4-dienes were highly stereoselective we synthesized a few insect pheromones. Bisbenzenesulfonylmethane 8 was condensed with 8-tetrahydropyranyloxyoctanal 9 [8] (CH_2Cl_2, piperidinium acetate, r.t., 24h) [2] to yield 85% of 10 and 15% of unchanged 8. Allylic 1,1-disulfone 10 was reduced to allylic sulfone 11 (84%) with aluminium amalgam as previously described [2]. The α-lithiated sulfone 11 was condensed with propanal (-35°C, 15h) and the product 12 (R=H) acetylated with acetic anhydride (DMAP, pyridine, r.t., 4h) [9] to give 75% of β-acetoxysulfone 12 (R=Ac)(erythro/threo : 44/56). Elimination of acetic acid with powdered sodium hydroxide [10] (ether, r.t., 6h) afforded 27% [1] of dienesulfone 1d, (R=-$(CH_2)_6$OTHP R^1=Et) (94% EE, 6% EZ) along with 57% of unchanged 12b [6]. After flash chromatography [4] 1d (> 99.5% EE) was treated with n-BuMgCl in the presence of 2% of $Ni(acac)_2$ to yield 49% of diene 3d R=$(CH_2)_6$ OTHP, R^1=Et). In this case the catalyst proved much more difficult to remove probably due to the THP ether group. After conversion (76%) into the corresponding acetate (HCl, MeOH, r.t., 3h followed by Ac_2O, DMA pyridine, r.t., 4h) the stereochemical composition of 3d (R^2=Ac) pheromone of *Lobesia botrana* (European grapevine moth) could be determined accurately and was found to be 95.1% 7E9Z [11]. For previous syntheses of 7E, 9Z-dodecadienyl acetate see reference 12.



In a similar way α-lithiated sulfone 13 was condensed with 9-tetrahydropyranyloxynonanal 14 [8] and the product acetylated in situ to give 72% of β-acetoxysulfone 15 (erythro/threo : 52/48). Acetic acid was eliminated as above (2eq. NaOH, ether, r.t. 2h) to afford 71% of dienesulfone 1e, (R=Et, R^1=$(CH_2)_8$ OTHP), 98% EE, which was isolated by flash chromatography in 49% yield and > 99.5% stereochemical purity. Hydrogenolysis of the sulfonyl group (n-BuMgCl 2% of $Ni(acac)_2$, THF ; 45% was followed by conversion into 9,11-tetradecadienyl acetate 3e (R=Et, R^1=$(CH_2)_8$OAc)(82%) pheromone of *Spodoptera littoralis* (Egyptian cotton leafworm). Capillary-glc indicated that the product contained 93% of the desired 9Z, 11E isomer. Previous syntheses of 9Z, 11E-tetradecadienyl acetate are given in reference 13.



Finally α-lithiated homoallylic sulfone 16 (>99% E)[3] was condensed with 9-tetrahydropyranyloxynonanal 14 to give 17 in 76% yield. Acetylation (Ac_2O, DMAP, pyridine, r.t., 4h, 92%)(erythro/threo : 56/44) and elimination of acetic acid (2eq. NaOH, dioxane, r.t., 15h) furnished dienesulfone 5b (R=$(CH_2)_8$ OTHP) (84%). After flash chromatography 5b (>99% EE) was reduced with sodium dithionite under phase transfer conditions (2eq. $Na_2S_2O_4$, 5eq. $NaHCO_3$, 2eq. Adogen [14], cyclohexane-H_2O 1/1, 80°C, 3.5h) to afford 65% of 6b (R=$(CH_2)_8$ OTHP). This diene was converted in a similar way into 9, 12-tetradecadienyl acetate, 6b, R=$(CH_2)_8$ OAc, pheromone of *Cadra cautella* (almond moth) and *Plodia interpunctalla* (Indian meal moth), containing > 97% of the 9Z, 12E-isomer and < 3% of 6b 9Z, 12Z. Previous preparations of 6b are collected in reference 15.

For comparative purposes the results of the β-elimination of acetic acid from unsaturated β-acetoxysulfones are collected in Table 2. The stereoselectivity, 94-98%, is slightly

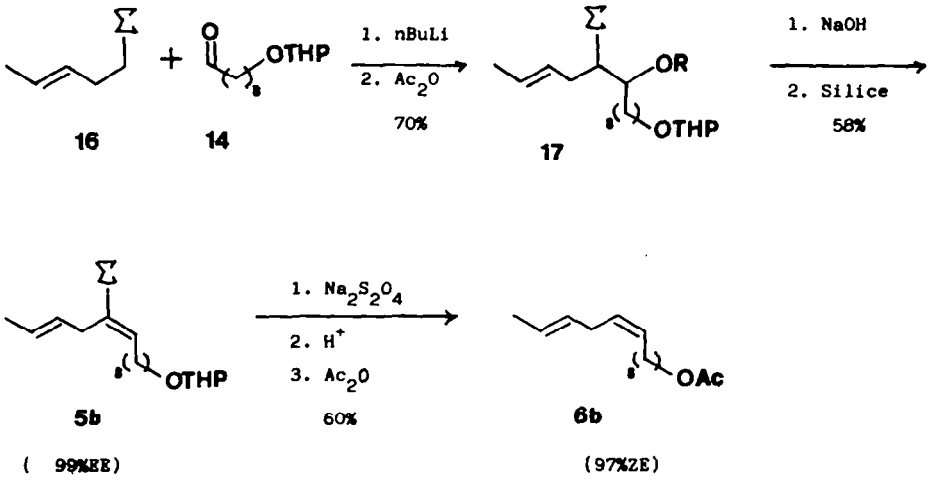
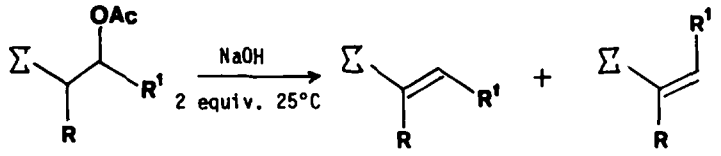
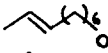
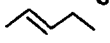
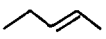


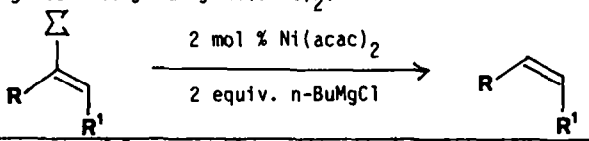
Table 2 : β-elimination of acetic acid from β-acetoxysulfones.

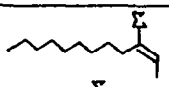
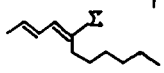
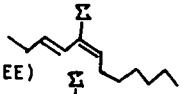
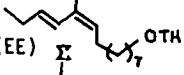
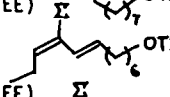
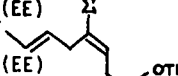
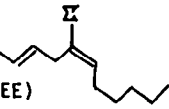


Entry	β-acetoxysulfones R	Compound	R'	(a) Time h	(b) Yield %	Compound	(c) Isomer ratio E	Z	(b) Secondary products %
ref.10	$-(CH_2)_3CH_3$	ref.10	$-CH_3$	15	85		100	0	15 hydroxysulfones
1		ref.1	$-(CH_2)_5CH_3$	6	67		96	4	5 β-acetoxysulfones
2		12	$-CH_2CH_3$	6	27	1d	94	6	57 β-acetoxysulfones
3		15	$-(CH_2)_8OTHP$	2	71	1e	98	2	
4		ref.1	$-(CH_2)_5CH_3$	15	67		97	3	
5	"	17	$-(CH_2)_8OTHP$	15	84	5b	96	4	

a) dioxane-ref.10, entries 4 and 5 ; ether entries 1 to 3. b) purified product. c) hplc.

Table 3 : Product distribution for various substrates in the reduction of vinylsulfones with Grignard reagents catalysed by $Ni(acac)_2$.



Entry	Substrate	Isomer ratio of starting sulfone	Isomer ratio of product	Compound	Yield %
ref.6a		99 (2E) 1 (2Z)	97.5 (2Z) 2.5 (2E)	ref.6a	70
1	 4EE	>95 (2E4E)	91 (2E4Z)	3c[f]	~15
2	 1b(EE)	98.5 (3E5E) 1 (3E5Z) 0.5 (3Z5E)	96 (3E5Z) 4 (3E5E)	3b	51
3	 1e(EE)	98.7 (9E11E) 1 (9Z11E) 0.3 (9E11Z)	93 (9Z11E) 5 (9E11E) 2 (9E11Z)	3e	35(e)
4	 1d(EE)	99 (7E9E) 1 (7E9Z)	95 (7E9Z) 4.5 (7E9E) 2 (7Z9E)	3d	37(e)
5	 5b(EE)	>98 (9E12E) 1 (9Z12E) <1 (9E12Z)	>90(d) (9Z12E)	6b[g]	24(e)
	" (a)	" " "	>85(d) (9Z12E)		16(e)[h]
6	 5a(EE)		>85(d) (2E5Z)	6a[i]	51

a) iPrMgCl. b) ^1H NMR or hplc. c) capillary-glc. d) minimum value (^1H NMR at 250MHz). e) after hydrolysis of ether group and acetylation. f) also 4% of undecenes; g) also 11% of butylated products. h) also 16% of butylated products 7b. i) also 19% of isopropylated products 7b. j) also 12% of butylated products 7a.

lower than that observed in the previously reported synthesis of vinylsulfones [10]. It is noteworthy that all dienesulfones were easily purified by flash chromatography [4]. Similarly the results of the reduction of dienesulfones with n-BuMgCl using 2% of $Ni(acac)_2$ as the catalyst are given in Table 3. Here again slightly lower stereoselectivity, ~95% is observed. Improvements in the removal of the catalyst will probably lead to an increase in stereochemical purity.

In the case of 2-benzenesulfonyl-1,4-dienes notable amounts of cross-coupling products are formed. The cross-coupling of vinylsulfones and Grignard reagents under $Fe(acac)_3$ catalysis has been described [16] whereas Nickel catalysis led mainly to hydrogenolysis [16]. Lehmkuhl and Coll. [17] have reported the stabilization of nickel complexes by a double bond in the 4 position. The cross-coupling reaction of dienesulfones 5 and i-PrMgCl has been optimized in another study [18].

The synthesis of E,Z-1,3-dienes [19] has been reviewed recently. The main approaches are the Wittig (Wittig-Horner) route and cross-coupling reactions of vinyl halides and alkenylmetals or alkynylmetals (followed by reduction of the triple bond). The latter techniques lead to conjugated dienes with 97-99% selectivity.

The methods recommended for the synthesis of 1,4-dienes are collected in reference 20. The majority of these methods lead to secondary products such as dimers, [20h] regioisomers [20eijl-q] or stereoisomers [20kp] or require elaborate starting materials [20t]. The stereoselective preparation of E,Z--1,3-dienes from E-allylic sulfones and E,Z-1,4-dienes from E-homoallylic sulfones should prove to be useful synthetic tools.

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

EXPERIMENTAL

Elemental analysis, which are collected in Table 6, were conducted at Paris VI, Centre de Spectrochimie. Analytical and preparative thinlayer chromatography (tlc) were performed on Merck PF 254 silica gel using eluent A (cyclohexane/dichloromethane/ethyl acetate : 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 B1500 Zorbax Sil. (4.6mmX25cm) column.

Spectra were recorded on the following : Bruker WP-80, Varian EM390 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 R10-10B for m/z. High resolution mass spectra were performed at Paris VI, Centre de Spectrochimie, on a AEI KRATOS MS50.

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 and n-butylmagnesium chloride were titrated with a solution of benzylic alcohol, 1N in toluene, using 2,2'-biquinoline [22] as the indicator prior to use. All reactions were run under a positive pressure of dry nitrogen.

1,1-Disulfones were prepared according to ref. 2 and dienesulfones were obtained by

the methods described in the preceding paper [1]. ω-Functionalized aldehydes 9 and 14 were prepared from 1,8-octanediol (22%) and 1,9-nonanediol (22%) according to a literature procedure [8]. Dienesulfones 1a, 1b and 5a were described in the preceding paper.

Reduction of sulfones with n-butylmagnesium chloride catalyzed by 2% of $Ni(acac)_2$: Typical procedure.

0.153mg (0.5mmol) of sulfone 1b and 2.6mg(0.01mmol) of $Ni(acac)_2$ were purged three times with nitrogen, 2.5ml of THF were added and the solution was stirred for 0.25h at room temperature. 1ml of n-butylmagnesium chloride (1N in THF) was added dropwise and the pale blue solution turned brown. Stirring was continued for 1h after which the solution was poured over a mixture of saturated aqueous ammonium chloride and ice. The aqueous layer was extracted 5 times with pentane and the combined organic layers were washed 5 times with water. After elution over a column of silica gel (Merck 7734 ; 25cm, 2cm in diameter), the solvent was distilled through a glass-bead column (30cm ; 2cm in diameter) yielding 44mg (51%) of 3E,5Z-dodecadienes 3b according to ^1H NMR (250MHz). Capillary-glc mass analysis indicated 2 isomers in a 97/3 ratio.

The aqueous layer was re-extracted with ether 5 times and the silica gel column was re-eluted with ether. The combined organic layers were dried, the solvent was distilled over the glass-bead column and the residue, 50mg, analyzed as above. The complex mixture of sulfones was separated into 3 fractions by preparative tlc (eluent : cyclohexane, dichloromethane/ethylacetate : 80/20/5) but attempts to identify these sulfones failed.

All reductions with Grignard reagents, catalyzed by transition-metal complexes, were performed in a similar way. In the case of compounds 3d and 3e, the silica gel column was replaced by an alumina plug (3cm ; 2cm in diameter) and solvents were removed at reduced pressure. Isomerization of 3,5-dodecadiene 3b was observed during distillation of the solvent on one occasion. It would appear that the catalyst and/or sulfur compounds formed during the reaction were responsible for this undesired reaction. When the separation of the catalyst (which forms a coloured band on the silica gel or alumina column) was successful this isomerization was avoided.

Reduction of sulfones with sodium dithionite under phase-transfer conditions : Typical Procedure.

174mg(1equiv.) of sodium dithionite and 210mg(2.5equiv.) of sodium hydrogen carbonate were added to a stirred mixture containing 306mg(1mmol) of 5a (>99%EE), 928mg(2equiv.) of Adogen 464, 5ml of cyclohexane and 5ml of water. The mixture was refluxed for 1h and then another 174mg (1equiv.) of reducing agent and 270mg(2.5equiv.) of base were added. The stirred suspension was refluxed for 17h and diluted with dichloromethane. The aqueous layer was extracted with the same solvent, the combined organic layers were washed with brine, dried and filtered. The solvent was distilled through the glass-bead column described above (at reduced pressure for 6b). Purification by vacuum chromatography [21] furnishes 118mg (64% of 2E,5Z-dodecadienes 6a, > 90% pure. ^1H NMR analysis indicated that compound 6a contains < 3% of the EE isomer (integration of the region at 2.6 to 2.7ppm).

All reductions with sodium dithionite were carried out in a similar manner and the procedure followed varied only in the reaction duration. This parameter has to be studied for each substrate as poor selectivity was observed with incomplete reactions.

[(2-Butene-1-ylidene heptyl)sulfonyl]benzene 4

217mg of [but-2-enylheptylidenebis (sulfonyl)]bisbenzene [3], 5ml of ether and 110mg (2equiv.) of potassium t-butoxide were stirred at room temperature for 5 minutes. 2ml of water were added followed by ether. After extracting the aqueous layer with ether the combined organic layers were washed with water, dried, filtered and evaporated at reduced pressure. Purification by flash chromatography [4] gave 75mg (80% pure ; 20% yield) of 4EE according to ^1H NMR analysis. (Spectral data for all sulfones are collected in Table 4).

Synthesis of 1-acetoxy-7,9-dodecadiene 3d, (R^2=Ac)

1,1-bisbenzenesulfonyl 9-[(tetrahydro-2H-pyran-2-yl)oxy] 2-nonene 10

5.92g(20mmol) of bisbenzenesulfonylmethane 8, 2.56g(20mmol) of 8-tetrahydropyranyloxyoctanal [9], 0.725g(5mmol) of piperidine acetate, 3g of molecular sieves (3A) and 150ml of dichloromethane were stirred at room temperature for 24h according to reference 2. Workup and purification by vacuum chromatography gave 9.49g of a mixture of 10(85%) and bisbenzenesulfonylmethane 8 (15%). An analytical sample of 10 was obtained by preparative tlc (eluent A). $C_{26}H_{34}O_6S_2$. Calc'd % C : 61.66, H : 6.72, S : 12.65. Obs'd % C : 61.40, H : 6.80,, S : 12.32.

9-Benzenesulfonyl-1-(tetrahydro-2H-pyran-2-yl)oxy -7-nonene 11

9.00g(19mmol) of the above 85/15 mixture of 10 and 8, 19ml of water, 361ml of THF and 9.6g(15equiv.) of Al-Hg were stirred at room temperature according to a known procedure [2]. Workup and vacuum chromatography gave a fraction containing 4.97g(84%) of 11 ($C_{20}H_{30}O_4S$) Calc'd % C : 65.57, H : 8.20, S : 8.74. Obs'd % C : 65.64, H: 8.12 , S : 8.43 followed by 0.4g(90%) of methylphenylsulfone identified by ^1H NMR [23].

Table 4 : Spectral data of sulfones.

Compound	IR	m/z	^{1}H NMR (250MHz) in $CDCl_3$: δ=0ppm for TMS, J in Hz
1d EE [bc]	1310,1140, 1080,1030,970	322,143,125,85, 68	1.03 to 2.50(m,21H), 3.28 to 4.04(m,4H), 4.62(br s, 1H), 5.28(m,2H), 6.97(t,1H,7.5), 7.41 to 8.03(m,5H)
1e ZE [d]		350,143,125,85	0.94(t,3H,7.5), 1.2 to 1.69(m,18H), 2.07(br q,2H, 6.8), 2.63(q,2H,7), 3.31 to 3.41(m,1H), 3.43 to 3.55 (m,1H), 3.63 to 3.77(m,1H), 3.81 to 3.93(m,1H), 4.57 (m,1H), 5.79 to 5.91(m,1H), 6.11 to 6.23(m,2H), 7.48 to 7.63(m,3H), 7.84 to 7.89(m,2H)
1e EE [e]		350,143,125,85	0.93(t,3H,7.5), 1.22 to 1.94(m,18H), 2.08(q,2H,7), 2.28(q,2H,7.5), 3.41(m,1H), 3.54(m,1H), 3.76(m,1H), 3.91(m,1H), 4.61(br t,1H,3), 5.91(br d,1H,16.5), 6.01 (dt,1H,J_1=16.5, J_2=5.7), 6.97(t,1H,7.5), 7.5 to 7.68 (m,3H), 7.84 to 7.91(m,2H)
2a E		252,111	0.86(t,3H,7), 0.92(t,3H,7), 1.16 to 1.86(m,4H), 1.97 (m,2H), 3.48(m,1H), 5.21(br dd,1H,J_1=15.5, J_2=9), 5.43(dt,1H,J_1=15.5, J_2=6.3), 7.54 to 7.72(m,3H), 7.85 to 7.92(m,2H)
2b [a]		309,167,143,125	0.78 to 0.88(m,6H), 1.1 to 1.4(m,13H), 1.58(m,2H), 1.94(m,2H), 2.06(m,1H), 3.4(m,1H), 5.17(ddt,1H,J_1= 15.5, J_2=9.5, J_3=1.4), 5.38(dt,1H,J_1=15.5, J_2=6.2), 7.48 to 7.66(m,3H), 7.8 to 7.85(m,2H)
4 EE [a]		292,207,150, 143,125	0.74 to 0.86(m,4H), 1.08 to 1.36(m,12H), 1.5 to 1.68 (m,2H), 1.86(d,3H,5.2), 2.18 to 2.28(m,2H), 6.13 to 6.32(m,2H), 7.29(m,1H), 7.47 to 7.63(m,3H), 7.83 to 7.91(m,2H)
5b	1300,1150, 1080,1030,970	350,279,236, 149,143,125	1.26 to 1.89(m,21H containing a dd at 1.43ppm, J_1= 6.2, J_2=1.5), 2.21(q,2H,7.4), 2.97(br d,2H,6.2), 3.36 to 3.59(m,2H), 3.72 to 3.95(m,2H), 4.61(m,1H), 5.09(dtq,1H,J_1=15, J_2=6.1, J_3=1.5), 5.19(dqt, 1H,J_1=15, J_2=6, J_3=1.5), 7.51 to 7.67(m,3H), 7.86 to 7.92(m,2H)
10 E [b]	1655,1325, 1165,1080, 1030,980	423,365,195, 143,125,85, 67,55	1.07 to 2.17(m,16H), 3.35 to 4.07(m,4H), 4.6(m,1H), 4.88(d,1H,10), 5.22 to 5.56(m,$AXBY_2$,2H,J_{AB}=15, J_{AY}= 10, J_{BX}=6), 7.47 to 8.09(m,10H)
11 E	1320,1150, 1080,1030,975	367,283,282, 281,226	1.14 to 2.09(m,16H), 3.34 to 4(m,6H containing a doublet at 3.8,J=7), 4.62(m,1H), 5.36 to 5.63(m,2H, J_{AB}=15), 7.56 to 7.77(m,3H), 7.89 to 7.97(m,2H)
12 (R=H) [b]	3450,1300, 1150,1085, 1035,980	423,282,143, 125,85	0.76 to 2.09(m,21H), 3.13 to 4(m,5H), 4.11 to 4.68 (m,2H containing a br singulet at 4.58), 4.96 to 5.79(m,2H), 7.4 to 8.06(m,5H)
12 (R=Ac) [b]	1740,1310, 1240,1150, 1080,1030, 970	466,465,383, 350,325,265, 181,163,143, 125	0.79 to 2.25(m,24H containing 2 singulets in a 44/ 56 ratio at 1.96 and 1.98ppm), 3.31 to 4.08(m,5H), 4.62(m,1H), 5.2 to 5.77(m,3H), 7.49 to 8.02(m,5H)
15 [b]	1720,1300, 1230,1140, 1080,970	269,227,143, 125	0.77 to 2.34(m,28H containing 2 singulets in a 48/ 52 ratio at 1.93 and 1.95ppm), 3.27 to 4.14(m,5H), 4.58(m,1H), 5.10 to 5.81(m,3H), 7.42 to 8.01(m,5H)
17 (R^2=H) [b]			1.19 to 2.10(m,28H), 2.37 to 2.68(m,2H), 2.99 to 4.38(m,7H), 4.62(m,1H), 5.08 to 5.69(m,2H), 7.53 to 8.12(m,5H)
17 (R^2=Ac) [b]	1740,1310, 1240,1150, 1080,1030	494,493,476, 465,411,268, 226,209	0.79 to 2.11(m,29H containing 2 singulets in a 44/ 56 ratio at 1.82 and 1.90ppm), 2.33 to 2.88(m,2H), 3.13 to 4.05(m,5H), 4.62(m,1H), 5.02 to 5.74(m,3H), 7.50 to 8.13(m,5H)

[a] impure. [b] ^{1}H NMR at 90MHz. [c] UV(cyclohexane) λ_{max}=227(ε=12000). [d] UV(cyclohexane) λ_{max}=222 (ε=16000) and for hplc λ=265(ε=5200). [e] UV(cyclohexane) λ_{max}=224 (ε=18000) and for hplc λ=265 (ε=3300).

ß-Hydroxysulfone 12 (R=H)

3.66g(10mmol) of sulfone 11 dissolved in 50ml of THF were treated with 7.5ml(1.2 equiv.) of n-butyllithium, 1.6N in hexane, at -78°C as described in the preceding paper. The temperature was allowed to rise to -35°C and stirring was maintained for 2h. 1ml(14mmol) of propanal was added and the stirred solution was maintained at -35°C for 15h. 1ml of a saturated aqueous solution of ammonium chloride was added at -35°C and THF was evaporated at reduced pressure. The residue was extracted with ether, washed with brine, dried and filtered. The solvent was evaporated and the oil obtained purified by vacuum chromatography to yield 3.90g(92%) of ß-hydroxysulfones 12 (R=H).

ß-Acetoxysulfone 12 (R=Ac)

3.39g(8mmol) of sulfone 12 (R=H) 1.6ml(16mmol) of acetic anhydride, 2.4ml(16mmol) of triethylamine and 32mg of 4-dimethylaminopyridine were mixed at 0°C and then stirred at room temperature for 4h. The solution was diluted with ether, washed with an aqueous solution of 10% NaOH followed by brine until neutral. The organic layer was dried, filtered and evaporated at reduced pressure. The residual oil was purified by vacuum chromatography to yield 0.205g of 1d (6.3%) EZ/EE 10.5/89.5, according to hplc (eluent : ethylacetate/2,2,4-trimethylpentane-10/90) and 3.02g(81%) of 12 (R=Ac) (threo/erythro, 56/44).

9-Benzenesulfonyl-1- (tetrahydro-2H-pyran-2-yl)oxy -7,9-dodecadiene 1d

2.80g(6mmol) of acetoxysulfone 12 (R=Ac), 0.48g of freshly-ground sodium hydroxide pellets and 30ml of ether, divided into 3 portions and placed in 3-25ml round-bottomed flasks were stirred at room temperature for 6h (heterogeneous). The suspensions were diluted with ether, united and washed with brine until neutral. The organic layer was dried, filtered, evaporated at reduced pressure and purified by flash chromatography (column, 9cmX15cm ; eluent, ethylacetate/2,2,4-trimethylpentane 10/90 → 20/80) to yield 605mg(25%) of 1d ($C_{23}H_{34}O_4S$) Calc'd % C : 67.98, H : 8.37, S : 7.88. Obs'd % C : 68.12, H : 8.68, S : 7.76 , containing > 99% of the EE isomer according to hplc analysis (the crude product contained 94.4% 1dEE and 5.6% 1dEZ) and 1.594g(57%) of ß-acetoxysulfone 12 (R=Ac).

1- (Tetrahydro-2H-pyran-2-yl)oxy -7,9-dodecadienes 3d

609mg(1.5mmol) of sulfone 1d EE (>99%), 7.8mg of $Ni(acac)_2$ (2%) 7.5ml of THF and 3ml of n-butylmagnesium chloride (1N in THF) were treated as above. Workup followed by vacuum chromatography led to 244mg (90% pure : 49%) of diene 3d.

Typical procedure for acid-catalyzed hydrolysis of the ether group and acetylation.

7E,9Z-Dodecadiene 1-ol 3d (R^2=H)

244mg(0.83mmol) of 3d (R^2=THP) 25ml of methanol and 5 drops of concentrated HCl were mixed at 0°C and stirred at room temperature for 2-5h. The reaction was monitored by tlc (eluent : ethylacetate-/pentane : 10/90). Methanol was evaporated at reduced pressure, the residue diluted with ether, washed with a 5% aqueous solution of sodium bicarbonate, followed by brine and dried. Evaporation of the solvent gave 160mg of 7,9-dodecadiene 1-ol 3d (R^2=H) which was acetylated without further purification.

1-Acetoxy 7E,9Z-dodecadiene 3d (R^2=Ac)

160mg(~0.8mmol) of alcohol 3d (R=H), 1.0ml of acetic anhydride, 1.5ml of triethylamine and 10mg of 4-dimethylamino pyridine were treated as above (acetylation of 12, R=H). Vacuum chromatography led to 143mg (>90% pure) of 3d (R^2=Ac). The overall yield from sulfone 1d was 38%.

The isomer ratio of 3d (R^2=Ac) was determined by comparison with authentic samples of all 4 isomers on a capillary-glc column, Table 3, entry 4 (50m, WCOT, 0.2mm, SE-52) [11].

Synthesis of 1-Acetoxy 9Z,11E-tetradecadiene 3e (R^2=Ac)

Acetoxysulfone 15

2.10g(10mmol) of (2-pentenyl)sulfonyl benzene 13, prepared according to ref.2 (>99.5%E), dissolved in 50ml of THF, were treated with 6.6ml of n-butyllithium (1.6N in hexane, 1.05 equiv.; -78°C→-35°C 2h) as previously described followed by 2.42g(10mmol;-35°C) of 9-tetrahydroxypyranyloxy nonanal 14. Stirring was continued for 5h and then 1.2ml(2mmol) of acetic anhydride were added dropwise at -35°C. The solution was maintained at -35°C for an additional 15h and hydrolyzed at this temperature with 1ml of a saturated aqueous solution of ammonium chloride. THF was evaporated in vacuo followed by the usual workup. After vacuum chromatography, < 5% of [(2-pentenyl)sulfonyl]benzene were recovered among a mixture of unidentified sulfones followed by 3.56g (87% pure ; 72%) of ß-acetoxysulfone 15 (threo/erythro : 52/48).

10-Benzenesulfonyl 1- (tetrahydro-2H-pyran-2-yl)oxy 9,11-tetradecadiene 1e

3.46g(7mmol) of acetoxysulfone 15, 0.56g of freshly-ground sodium hydroxide and 35ml of ether divided among 3-25ml round-bottomed flasks were treated as above. Workup and purification by flash chromatography gave 35mg(1%) of 1e ZE and 2.15g(71%) of 1e EE (>99.5%). $C_{25}H_{38}O_4S$. Calc'd % C : 69.12, H 8.76, S : 7.37. Obs'd % C : 69.44, H : 9.12, S : 7.56.

Table 5 : Spectral data of olefinic compounds and ω-functionalized aldehydes.

Compound	m/z	^{1}HNMR(250MHz) in $COCl_3$: δ=0ppm for TMS, J in Hz	HR(m/z)or references
3b EZ	166(100), 137(1), 123(3) 109(9),95(56),82(66),81 (39),67(100)	0.91(m,3H), 1.04(t,3H,7.5), 1.22 to 1.45(m, 8H), 2.08 to 2.24(m,4H), 5.35(m,1H), 5.64(br dt,1H,J_1=15, J_2=6.7), 6.01(br t,1H,11), 6.37(br ddd,J_1=15, J_2=11, J_3=1.5)	166.1721 for 166.17215
3c EZ[a]			7
3d(R^2=THP)[ab]	(NH_3) : 284,267 (e.i.) : 122,105,85,58	0.99 to 2.33(m,24H), 3.29 to 4.10(m,4H), 4.63 (m,1H), 5.18 to 6.18(m,3H), 6.37(dd,1H,J_1= 15, J_2=10)	
3d(R^2=H)[ab]		0.99 to 2.33(m,20H), 3.59(t,2H,6), 5.11 to 6.08(m,3H), 6.28(dd,1H,J_1=15, J_2=10)	12c,j
3d(R^2=Ac)[a]	225(15),224(100),164(15), 149(4),136(17),135(49), 123(5),122(13),121(50), 108(26),107(26),96(26), 95(59),94(26),93(56),91 (26),82(39),81(28),80 (21),79(73),69(21),68 (13),67(58)	1.00(t,3H,7.5), 1.24 to 1.28(m,8H), 1.53 to 1.69(m,2H), 1.95 to 2.25(m,7H containing a singulet at 2.05 for 3H), 4.07(t,2H,6.7), 5.33(dt,1H,J_1=11, J_2=7.5), 5.67(q,1H,7.5-simplifies to a doublet, J_{AB}=15), 5.95(br t,H,11), 6.34(ddd,1H,J_1=15, J_2=11, J_3=1)	12a
3e(R^2=THP)[a]		1.03(t,3H,7.4), 1.33(m,12H), 1.47 to 1.91(m, 10H), 2.05 to 2.23(m,4H), 3.41(m,1H), 3.53(m, 1H), 3.76(1H), 3.90(m,1H), 4.62(br t,1H,3), 5.34(br dt,1H,J_1=11, J_2=7.5) 5.74(br dt, 1H,J_1=15, J_2=6.5), 6.01(br t,1H,11), 6.36 (dd,1H,J_1=15, J_2=11)	
3e(R^2=H)[ab]		1.02(t,3H,7.5), 1.13 to 1.79(m,18H), 1.91 to 2.37(m,5H), 3.64(t,2H,6.5), 5.34(dt,1H,J_1= 10.5), J_2=7.5), 5.52 to 6.17(m,2H), 6.36 (dd,1H,J_1=15, J_2=10.5)	12c
3e(R^2=Ac)[ab]	252(4), 192(1), 164(1), 163(2),149(3),136(3), 135(7), 124(3), 123(3), 122(6),121(12),110(9), 109(7),108(7),107(8),96 (14),95(22),94(12),93 (18),91(6),82(29),81(31), 80(19),79(45),77(10),69 (14),68(27),67(100)	0.98(t,3H,7.5), 1.12 to 1.83(m,14H), 1.83 to 2.32(m,7H containing a singulet at 2.00ppm), 4.06(t,2H,6.3), 5.29(dt,1H,J_1=10.5, J_2= 7.5), 5.48 to 6.13(m,2H), 6.32(dd,1H,J_1= 15.5, J_2=11)	12h
6a EZ	166,124,123,110,109,95, 82,81,79,77,69,68,67,55	0.84(m,3H), 1.15 to 1.39(m,8H), 1.61(dt,3H, J_1=4.5, J_2=1.5), 2.0(br q,2H,6.5), 2.70 (m,2H), 5.3 to 5.53(m,4H)	166.1721 for 166.17215
6b(R=THP)		1.23 to 1.90(m,21H), 2.03(br q,2H,6.2), 2.72 (m,2H), 3.34 to 3.46(m,1H), 3.46 to 3.58(m, 1H), 3.68 to 3.8(m,1H), 3.84 to 3.95(m,1H), 4.6(br t,1H,3), 5.32 to 5.54(m,4H)	
6b(R=H)		1.18 to 1.78(m,16H), 2.03(m,2H,6.3), 2.73(m, 2H), 3.66(t,2H,6.6), 5.33 to 5.56(m,4H)	
6b EZ (R=Ac)	252(1),182(11),164(3), 163(3),149(5),131(5),130 (11),124(6),123(5),122 (8),121(21),110(19),109 (13),108(15),107(21),96 (25),95(42),94(31),93 (32),82(46),81(65),80 (26),79(62),69(26),68 (62),67(85),55(100)	1.20 to 1.42(m,10H), 1.54 to 1.7(m,5H), 1.98 to 2.09(m,5H containing a singulet at 2.06ppm), 2.72(m,2H), 4.06(t,2H,6.3), 5.32 to 5.54(m,4H)	15b
6b EE (R=Ac)		1.17 to 1.47(m,10H), 1.51 to 1.73(m,5H), 1.91 to 2.09(m,5H containing a singulet at 2.05), 2.72(m,0.4H), 4.05(t,2H,6.7), 5.33 to 5.53(m,4H)	2.62(m,1,6H),
9		1.21 to 1.95(m,16H), 2.44(td,2H,J_1=7.2, J_2=1), 3.29 to 4.17(m,4H), 4.62(m,1H) 9.85(t,1H,1.2)	8
14		1.1 to 2(m,18H), 2.4(td,2H,J_1=7.2, J_2=1), 3.2 to 4.07(m,4H), 4.57(m,1H), 9.8(t,1H,1)	24

[a] chemical purity < 100%. [b] ^{1}H NMR at 90MHz.

1-(tetrahydro-2H-pyran-2-yl)oxy 9,11-tetradecadienes 3e (R^2=THP)

870mg(2mmol) of 1e, 10.5mg of $Ni(acac)_2$(2%), 10ml of THF and 4ml of n-butylmagnesium chloride, 1N in THF, are treated in the usual way to yield 282mg(90% pure ; 48% of 3e (R^2=THP) and 200mg of unidentified sulfone.

1-Acetoxy 9Z,11E-tetradecadiene 3e (R^2=Ac)

282mg(0.9mmol) of 3e R^2=THP were treated with 25ml of methanol and 5 drops of concentrated HCl to yield 200mg of 3e R^2=H. Acetylation with 1ml of acetic anhydride, 1.5ml of triethylamine and 10mg of 4-dimethylaminopyridine as above gave after vacuum chromatography 207mg (90% pure) of 3e (R^2=Ac). The overall yield from 1e was 37%. The isomer ratio was determined as for 3d.

Synthesis of 1-acetoxy 9Z,12E-tetradecadiene 6b (R^2=Ac)

β-Hydroxysulfone 17 (R=H)

2.10g(10mmol) of [(3-pentenyl)sulfonyl]benzene 16, prepared according to ref.3 (>99%E), dissolved in 50ml of THF were treated first with 6.6ml(1.05equiv.) of n-butyllithium, 1,6N in hexane(-78°C, ↗ 0°C, 0.5h, ↘ -35°C) followed by 2.42g(10mmol) of 9-tetrahydroxypyranyloxynonanal 14 at -35°C. Workup and vacuum chromatography as described previously gave 3.43g(76%) of β-hydroxysulfone 17 (R=H).

β-Acetoxysulfone 17 (R=Ac)

Acetylation of 2.77g(6.1mmol) of sulfone 17 (R=H) with 7.5ml(75mmol) of acetic anhydride, 9ml(60mmol) of triethylamine and 30mg of 4-dimethylaminopyridine as previously described gave 2.79g(92%) of sulfone 17 (R=Ac) (threo/erythro : 56/44).

10-Benzenesulfonyl 1-(tetrahydro-2H-pyran-2-yl)oxy 9,12-tetradecadiene 5b (R^2=THP)

2.79g(5.65mmol) of acetoxysulfone 17 (R=Ac) were stirred at room temperature for 15h with 0.44g(2equiv.) of freshly-ground sodium hydroxide and 25ml of dioxane. After the usual work up purification by flash chromatography yielded 1.4g(69%) of 5b (R^2=THP) >99%EE according to hplc analysis. $C_{25}H_{38}O_4S$. Calc'd % C : 69.12, H : 8.76, S : 7.37. Obs'd % C : 69.13, H : 8.98, S : 7.01.

1-[(Tetrahydro-2H-pyran-2-yl)oxy] 9Z,12E-tetradecadiene 6b (R^2=THP)

217mg(0.5mmol) of 5b R^2=THP (> 99%EE) were treated with 464mg(2equiv.) of Adogen 464, 2.5ml of cyclohexane, 2.5ml of water, 174mg(2equiv.) of sodium dithionite and 210mg(5equiv.) of sodium bicarbonate for a total of 3.5h at reflux temperature as described in the typical procedure. Workup and vacuum chromatography gave 96mg (65%) of 6b (R^2=THP).

1-Acetoxy 9Z,12E-tetradecadiene 6b (R^2=Ac)

The ether protecting group of 6b (R^2=THP) (96mg) was removed as above (8ml of MeOH, 5 drops of conc. HCl) followed by acetylation (1ml of Ac_2O, 1.5ml of Et_3N, 10mg of DMAP) to give 81mg of 6b R^2=Ac. The overall yield from 5b was 60% and capillary-glc (50m WCOT interior diameter 0.23, CPSIL 83, pHe=0.9 bar, 160°C) indicated that the product contained 97% of 6b (R^2=Ac, 9Z,12E) and 3% of 6b (R^2=Ac 9Z,12Z) by comparison with authentic samples of all 4 isomers.

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